ANALYSIS OF ACTINIDES IN SAFEGUARDS SWIPE SAMPLES BY RADIOMETRIC AND MASS SPECTROMETRIC METHODS

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Ph.D. Dissertation

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Contents

1. Introduction

The safeguards system of the International Atomic Energy Agency (IAEA) aims to prevent the diversion of nuclear material from peaceful uses to nuclear weapons or other nuclear explosive devices. Wide range of safeguards measures (e.g. maintenance of the system of accounting for and control of nuclear material, containment and surveillance, inspections, in-situ non-destructive measurements of nuclear material, collection of environmental samples…) have been implemented to confirm the peaceful uses of the declared activities and material and to discover clandestine activities at nuclear facilities of non-nuclear-weapon states which are parties to the Safeguards Agreements.

Swipe sampling as the most effective type of environmental sampling has been routinely used by safeguards inspectors since 1996. Its objective is to discover the traces of undeclared nuclear activities and/or material through the detection of U and Pu in the samples performed by either bulk or particle analysis.

The U and Pu content of the safeguards samples is usually measured - after the separation of actinides - by mass spectrometric techniques (such as inductively coupled plasma mass spectrometry (ICP-MS), thermal ionization mass spectrometry (TIMS)) in bulk analysis, however radiometric methods - such as alpha spectrometry - are capable of determining actinides, as well. Although the combination of these techniques and the determination of other actinides (Th, Np, Am) are only rarely performed especially for safeguards purposes, it could not only improve the reliability of the results (through the comparison of the results on isotopes which can be analyzed by both techniques) but more information could also be obtained (there are many isotopes which can be analyzed by only one technique).

Bulk analysis provides information only about the average composition of the samples however the artificial fissile material in the environment mostly occurs in the form of solid, radioactive particles. Particles containing alpha emitting and/or fissile material can be identified, localized and even micro-manipulated. The U content of these 'hot particles' originating from swipe samples can be examined with high sensitivity excluding the effect of the sample as matrix. The information on single particles (such as isotope ratios of actinides) given by particle analysis offers a great possibility. According to the results, various origin scenarios of particles can be distinguished in the same swipe sample, furthermore traces of undeclared activities can be detected even in case of attempts of concealments (e.g. releasing

big amount of declared material on site). Moreover, the more precise information can improve the verification process of IAEA Safeguards.

The aim of this study was to develop sensitive radioanalytical methods for bulk and particle analysis of safeguards swipe samples to determine the actinides in the whole sample or the U isotopic composition in radioactive particles originating from swipes using alpha spectrometry and ICP-MS.

The experimental work of the dissertation covers two topics: development of radioanalytical procedures for (1) the determination of actinides by alpha spectrometry and/or ICP-MS and (2) the determination of U isotopic composition of single particles originating from safeguards swipe samples by laser ablation ICP-MS (LA-ICP-MS).

The chapters on bulk analysis describe (1) the adaptation of a radiochemical separation method for the determination of actinides (Th, U, Pu, Am) by alpha spectrometry in safeguards swipe samples and its application in the analysis of real swipe samples taken in Hungarian nuclear facilities for national safeguards purposes; (2) the improvement of this radioanalytical procedure which resulted in the capability of the sequential separation of all the actinides (Th, U, Np, Pu and Am(Cm)) using one single TRU extraction chromatographic column and their measurement both by alpha spectrometry and ICP-MS; (3) the modification of the standard procedure of the IAEA for the determination of U and Pu in environmental samples to be able to analyze low level ^{238}Pu in swipe samples. The chapter on particle analysis describes procedures developed for the determination of U isotopic composition of single particles originating from safeguards swipe samples by LA-ICP-MS.

2. Literature

This chapter, the literature overview discusses the main fields related to my research topic. Since the literature of analytical techniques applied for safeguards purposes and especially that of actinide separation and determination is huge the present summary tries to give a very brief overview on general aspects and focuses on special aspects of the topics that are closely related to the subject of this study. First, the safeguards system of the International Atomic Energy Agency as the base of the current dissertation is shortly discussed from the practical point of view of the analysis of safeguards swipe samples. Secondly, the important properties of the actinides relevant to their separation are shortly discussed. After the short description of the actinide separation techniques, a literature review on the sequential separation of actinides is given followed by a very brief summary of the applied measurement techniques including alpha, beta (liquid scintillation counting), gamma spectrometry and mass spectrometry. The particle analysis of actinides are also discussed. The particle analysis as a new tool of safeguards analyses is described following the logical order of the major steps: (1) removal of particles from the original media, (2) identification of particles of interest, (3) localization and relocalization and (4) determination of the isotopic composition of single particles.

2.1. The safeguards system of the International Atomic Energy Agency

2.1.1. Traditional and strengthened safeguards system

The main objectives of the Nuclear Non-proliferation Treaty (NPT, 1968) are to prevent the spread of nuclear weapons and nuclear weapon technologies, to further the goal of nuclear disarmament and to ensure the exchange of scientific information on the applications of atomic energy for peaceful purposes. [NPT]

According to the Article III of the NPT, the traditional safeguards system of the International Atomic Energy Agency was established whose main objective is to prevent the diversion of nuclear material from peaceful uses to nuclear weapons or other nuclear explosive devices. In other words the safeguards system has to explore the diversion (or the attempt of the diversion) before the nuclear weapon can be built. The so-called significant quantity (SQ) (needed to build a nuclear weapon) and the time factor (needed for the production of the given nuclear material) besides the probability of drawing false conclusion have been determined for each nuclear material known by safeguards goals (to be able to detect significant quantity of undeclared nuclear material within the time factor with less than

5% of probability of false conclusion). (Table 1) [Janssens 2007] The implemented safeguards measures include e.g. (1) establishment and maintenance of a system of accounting for and control of nuclear material by the states, (2) the submission of reports on all nuclear materials (subjected to safeguards) to the IAEA by the states, (3) the system of containment and surveillance established by the IAEA in nuclear facilities and (4) the inspection of the IAEA including visual observation, counting of nuclear material, installing and control of seals and surveillance systems inside the facilities to ensure the continuous control, non-destructive analysis and collection of environmental and nuclear material samples. [NPT, SGA]

These so-called traditional safeguards measures have been established according to the three safeguards goals. This system can "only" verify that no diversion of nuclear material from declared activities has taken place and the reports of the nuclear facilities submitted by the states are correct.

Table 1 'The three safeguards goals' [Janssens 2007]

	Low-enriched U	Highly enriched U	^{233}U	Pu	Th
SQ [kg]	75	25	8	8	20 000
Time factor	1 year	1 month	1 month	1 month	1 year
Probability for false conclusion	< 5%	< 5%	< 5%	< 5%	< 5%

In the 1990's in Iraq undeclared nuclear activities were discovered by safeguards inspectors. This issue pointed out the main weak point of the traditional safeguards system: only declared activities are controlled. The strengthening of the safeguards system was decided to make it capable of discovering undeclared nuclear activities, as well. The Additional Protocol [AddProt] (1997) summarizes the modifications in the safeguards measures: e.g. (1) the area of the accounting system has been widened (more information is needed to report, more facilities and all quantities of nuclear material are under the Safeguards Agreements), (2) the notification procedures of the inspections have been changed, (3) there are changes in the inspections, as well (more tools: e.g. use of satellites and open-source information, extended environmental sampling; more locations). Thus the strengthened safeguards system can verify not only the correctness but the completeness of the reports submitted by the states and it is able to discover undeclared nuclear activities, as well. [AddProt, Donohue 1998, Janssens 2007]

2.1.2. Environmental sampling for safeguards purposes

As it was mentioned before the aim of the environmental sampling for safeguards purposes is to verify that there are no undeclared nuclear activities in states under the Safeguards Agreements. This is somewhat illogical, since the absence of the proof cannot be the proof of the absence. Although in the point of view of the following statement it makes sense: All the nuclear activities including the declared ones must have emission to the environment which characterizes the activity and these traces can be identified by environmental sampling and analysis.

There are two types of environmental sampling for safeguards purposes: wide area and location-specific. The principles and the procedures for the first type still have been under development. The latter type has already been used as a routine safeguards measure. [AddProt]

Swipe samples are part of the second type besides air, water, plants and soil samples which are taken from inside or outside of the given nuclear facility. Swipe sampling as the most efficient environmental sampling tool was introduced into the routine safeguards measures by the Program "93+2" whose aim was to strengthen the IAEA safeguards system. [Donohue 1998] The safeguards swipe samples are so-called ultraclean cotton materials with a size of 10 mm × 10 mm. Safeguards inspectors wipe a given surface with them according to a protocol. Afterwards these samples in sealed, double-packed plastic bags are transported to the Safeguards Analytical Laboratories and analyzed there and in the laboratories of the Network of Analytical Laboratories (NWAL) to have independent results to increase reliability. [IAEA 2003]

Swipe sampling (and other environmental sampling methods) can be used as an effective safeguards measure if the following assumptions are taken into account. (1) Nuclear activities (like any activities) have emission to the environment. Several kilograms of weapon-grade U or Pu are needed to build a nuclear weapon. On the contrary the analytical techniques used for the analysis of environmental samples for safeguards purposes have detection limits in the level of nano-, pico- or even femtograms. This fact gives a relatively high probability to collect traces of the emission of undeclared activity with swipe samples and to detect them with sensitive and selective analytical methods. (2) The isotopic composition of the emitted material is characterized by the undeclared activity. (3) The content of the swipe samples characterizes the emitted material. (4) There are also some procedures which can be used to clean or mask the traces of undeclared activities: cleaning, swamping and spiking. These

procedures cannot be effective enough to remove all the traces of the emission or to mask it completely. Moreover applying these procedures is also suspicious and particle analysis can be effectively used against these procedures since it can distinguish particles with different isotopic composition from the same sample. (5) The material originating from declared and undeclared activities can be distinguished according to not only the isotopic composition but also comparing the results of the analysis with the reports submitted by the states. This comparison is reliable only if the reports are complete and correct. [Donohue 2003]

The environmental samples are analyzed in the Clean Laboratory of the Safeguards Analytical Laboratories (specialized for safeguards analysis and equipped with state-of-the-art analytical instruments) in order to determine the following information: (1) U and Pu concentration and isotopic composition, (2) the ratio of Am and Pu isotopes, (3) U and Pu isotopic composition of single particles in case of particle analysis. [Donohue 2003]

The environmental samples first of all are screened by gamma spectrometry to detect fission and decay products and by X-ray fluorescence spectrometry to detect the presence of U and Pu. The samples can be measured by alpha spectrometry and/or beta counting, as well. Afterwards the samples are examined by either bulk (ICP-MS, TIMS) [Vogt 2001] or particle analysis (scanning electron microscopy (SEM), SIMS, FT/TIMS). The analytical method is chosen according to the results of the screening procedures. [IAEA 2003]

2.1.3. The standard procedure of the IAEA Clean Laboratory for the determination of U and Pu in environmental samples

In the Clean Laboratory Unit of the Safeguards Analytical Laboratory the U and Pu content of environmental samples is determined by a complex radioanalytical procedure (shown in Fig. 1) based on ion exchange and extraction chromatography [Attrep 1992, Shinonaga 2008].

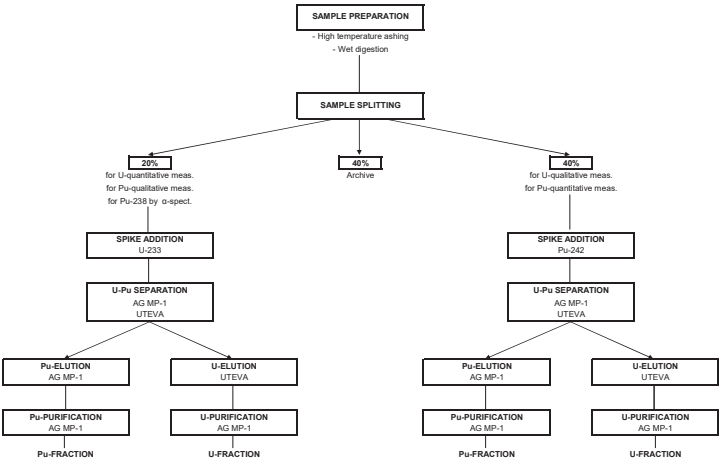

Fig. 1 The flowchart of the procedure for the determination of uranium and plutonium in swipe samples

After ashing and acid digestion of the sample, the master solution is divided into three parts for (1) U quantitative analysis (U IDA: isotope dilution analysis) and Pu isotope ratio (Pu ISO: isotope ratio analysis) determination; (2) for Pu quantitative analysis (Pu IDA) and U isotope ratio (U ISO) determination and (3) for archive. The tracers of ^{233}U and ^{242}Pu are added to the sample aliquot for U and Pu isotope dilution mass spectrometry, respectively (U IDA and Pu IDA). No tracers are used for isotope ratio measurements. After spiking, U and Pu are separated on a stacked two-column system of AG MP-M1® anion exchange and UTEVA® extraction chromatographic columns. Uranium and Pu fractions are eluted from the separated UTEVA and AG MP-M1® anion exchange columns, respectively followed by further purification of the fractions using anion exchange AG MP-M1® resin (U and Pu) or TEVA® extraction chromatographic resin (Pu). The final purified fractions of U and Pu are measured by ICP-MS and/or TIMS. [Mácsik 2010]

2.1.4. The importance of the isotopic composition of actinides for safeguards purposes

Nuclear material is usually characterized by its U and/or Pu isotopic composition; therefore the IAEA safeguards inspection samples (e.g. swipe samples) are analyzed in order to detect U and Pu isotopes.

Depleted, natural, low enriched, highly enriched and weapon grade U can be distinguished according to the isotopic composition of ^{235}U/U (Table 2). Non-irradiated U contains only

naturally occurring U isotopes (^{234}U, ^{235}U and ^{238}U), therefore ^{236}U can be considered as a signature of irradiated (reprocessed) U. Plutonium is graded according to the isotopic composition of ^{240}Pu/^{239}Pu: reactor, fresh fuel, weapon and super grade (Table 2).

Table 2 The grades of U and Pu [Warneke 2002]

Type of grades	Uranium ^{235}U/U		Plutonium ^{240}Pu/^{239}Pu
Depleted	<0.71%	**Reactor grade**	>19%
Natural	0.71%	**Fuel grade**	7% - 19%
Low enriched	0.71% - 20%	**Weapon grade**	<7%
Highly enriched	>20%	**Super grade**	<3%
Weapon grade	>90%		

The knowledge of the isotopic composition of U and Pu is important not only because weapon grade nuclear material can be discovered but the declared nuclear activities of the given nuclear facility can also be checked. The reactor type determines the nuclear fuel type (e.g. light water power reactors use low enriched U (usually 3...5% ^{235}U/U) while heavy water reactors can operate with natural U). The isotopic composition of spent fuel can vary in a wide range depending on the reactor type (e.g. heavy- or light water reactor), the fresh fuel composition, the coolant and moderator system and the burn-up level [Warneke 2002, Carlson 1997]. Reactor grade Pu is usually produced by light or heavy water reactors at a burn-up level which indicates peaceful uses (power production). Fuel grade Pu originates usually from tritium production reactors (e.g. special heavy water-moderated reactors, power reactors with fuel rods containing Li replacing the usual control rods) but power reactors can also create it after only about 1 year of fuel irradiation ('medium' burn-up). Weapon grade Pu can be produced through irradiation of ^{238}U by fast neutrons, so the optimal condition involves short irradiation time, natural or only slightly enriched U as fuel. These conditions can be found e.g. in fast breeder reactors or in heavy water- or graphite-moderated production reactors (e.g. RBMK reactors). [Carlson 1997] Power reactors can also produce weapon and super grade Pu in case of very short irradiation time.

The isotopic composition of other actinides can also provide useful information on nuclear material. The neutron flux and the availability of neutrons are different in nuclear reactors operating for weapon grade Pu production or in ones run as power reactors. Reactor and fuel grade Pu contain significantly higher amount of not only ^{240}Pu but other activation products and their decay products and the activation products of these isotopes (e.g. ^{241}Pu, ^{241}Am, ^{237}Np, ^{242}Cm and ^{244}Cm).

2.2. Actinides

2.2.1. Generation and sources of actinides

Actinides are the groups of 15 elements in the f block of the periodic table of elements from ^{89}Ac to ^{103}Lr. They can be divided into two groups according to their origin. Light actinides (Ac, Th, Pa and U) are members of the natural decay series (^{238}U, ^{235}U and ^{232}Th decay series) except the isotope of ^{236}U which is artificial: it is generated in nuclear fuel through neutron activation of ^{235}U. The concentration of Th and U in the Earth's crust is relatively high: 8.1 ppm and 2.3 ppm, respectively contrary to those of Ac and Pa which are small. [Lehto 2011] Uranium (natural and enriched) is used as fuel in nuclear reactors (nuclear power plants and research reactors). Depleted U can be used for shielding or in missiles due to its high density. Thorium-232 is considered as an alternative nuclear fuel: fissile ^{233}U is produced by neutron activation of ^{232}Th.

The second group contains the transuranium elements known as heavy actinides (Np, Pu, Am, Cm, etc.). They are formed in nuclear reactors (Fig. 2) and explosions through neutron captures and alpha and beta decays. The amount of produced transuranics is larger in reactors than in explosions due to the longer neutron irradiation. Plutonium (^{239}Pu) as nuclear weapon material has been produced for nuclear explosive devices and all the Pu isotopes can be found in spent nuclear fuel. Plutonium isotopes occur also in the environment due to nuclear weapon tests, nuclear accidents (e.g. Chernobyl) and they can be naturally produced, as well through the activation of U by neutrons from cosmic rays or from spontaneous fission of ^{235}U. The amount of Np, Am and Cm produced in nuclear reactors is approximately one tenth of that of the Pu in reactors. Elements heavier than Cm really rarely occur not only in the environment but even in nuclear wastes or spent fuel. [Choppin 2001, Lehto 2011]

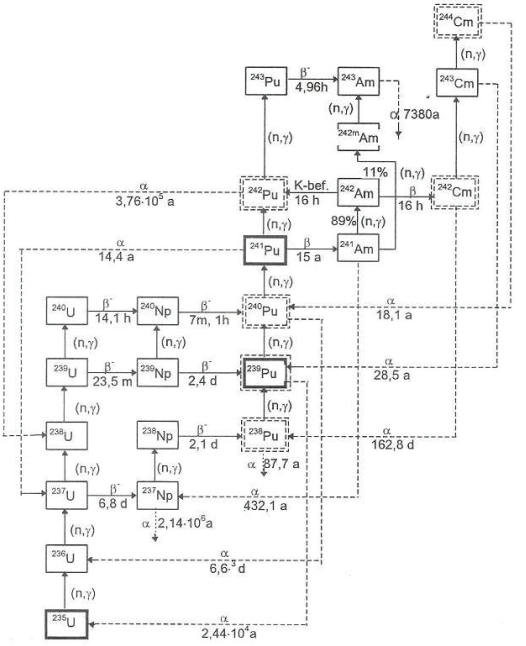

Fig. 2 The process of actinide generation in the nuclear fuel of light water reactors [Csom 1997]

2.2.2. Electronic configuration of actinides

Actinides have four completely filled inner electronic shells: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, (K, L, M, N) and three partly empty outer electronic shells: 6d, 7s and 5f (O, P, Q). The chemical behavior of actinides is characterized mainly by the filling of the seven 5f orbitals. The light actinides from Th up to Am behave quite different from lanthanides since the electrons of 5f orbitals also take part in chemical bonding: they readily form complexes and covalent bonds. The chemistry of Th, Pa, U, Np and Pu is similar to that of the d-transition elements. Heavier actinides (from Am) and Ac behave much more similar to lanthanides because 5f electrons usually do not take part in chemical bonding: they form mostly ionic bonds. [Choppin 2001, Lehto 2011]

2.2.3. Oxidation states of actinides

The chemical behavior of actinides depends highly on their *oxidation states* which vary between +II and +VII. Thus in many radiochemical procedures adjusting the oxidation states

of actinides is the first crucial step. Table 3 summarizes the possible oxidation states of actinides. The most typical oxidation states of Ac, Th, Pa, U, Np and Pu are +III, +IV, +V, +VI, +V and +IV, respectively, and +III for actinides heavier than Pu, except in case of No where the most stable oxidation state is +II. In aqueous solutions there is only one possible oxidation state for Th (IV) and Cm (III). However, Am can occur in many oxidation states (e.g. even in +VI) in aqueous solutions, these states except Am(III) are highly unstable [Osváth 2009]. [Choppin 2001, Lehto 2011]

Table 3 The possible oxidation states of the investigated actinides [Choppin 2001, Lehto 2011]

	+II	+III	+IV	+V	+VI	+VII
Thorium		x	**X**			
Uranium		x	x	x	**X**	
Neptunium		x	x	**X**	x	x
Plutonium		x	**X**	x	x	x
Americium	(x)	**X**	x	x	x	

X: most typical, x: possible, (x): only in solid-state compounds

Also the *form* of actinides (An) depends on their oxidation states. While in the oxidation state of +III and +IV they form simple cations: An^{3+} and An^{4+}, and in the oxidation state of +V and +VI they occur as complex actinyl ions: AnO_2^{+}, AnO_2^{2+}. [Lehto 2011]

There are separation techniques for actinides based on the phenomenon of *complex formation* (liquid-liquid extraction, extraction chromatography). Actinides can form a large variety of complexes with e.g. inorganic monovalent (e.g. F^{-}, Cl^{-}), divalent (e.g. CO_3^{2-}) ligands, inorganic and organic phosphates (e.g. tributyl phosphate (TBP)). The strength of complexes formed with inorganic monovalent ligands decreases in the following order: $F^{-} > NO_3^{-} > Cl^{-} > ClO_4^{-}$. In case of a given actinide the stability of the formed complex is decreasing with the following order of the oxidation state: +IV > +VI > +III > +V [Choppin 1997]. [Lehto 2011]

A great variety of applied redox reagents for the *oxidation state adjustment* of the actinides has been described in the literature. In the followings the most commonly used procedures for oxidation state adjustment – that can be used for extraction chromatography – will be summarized. The oxidation state of Th and Am is usually not adjusted. They are considered being +IV and +III, respectively. Osváth et al tried to adjust Am(VI) to be able to separate it on an extraction chromatographic resin (UTEVA®). The oxidation state adjustment

itself was successful but the separation of Am was not since the Am(VI) turned to Am(III) as soon as it was loaded onto the column. [Osváth 2009]

The oxidation state adjustment of Pu and Np is well studied. The oxidation state of Pu changes really easily and it can occur in two or three oxidation states in the same solution at the same time due to disproportion. [Lehto 2011] The most stable oxidation state of Np is +V which cannot be retained by any extraction chromatographic material. Therefore for its separation first it has to be adjusted to +IV or +VI.

The oxidation state of Pu can be adjusted to +III, +IV or +VI. Several redox reagents can be used for the reduction of Pu to Pu(III): hydroquinone [Horwitz 1993], NH_2OH [Horwitz 1993], Mohr's salt ($(NH_4)_2Fe(SO_4)_2 \times 6H_2O$) [Hrnecek 2005, Perna 2001, Vajda 2009], semicarbazide [Grate 1998], ascorbic acid [Grate 1998], $SnCl_2$ [Grate 1998], NaI [Grate 1998], $TiCl_3$ [Grate 1998, Vajda 2009, Truscott 2001], ferrous sulfamate [Thakkar 2002], mixture of ferrous sulfamate and ascorbic acid [Grate 1998], mixture of sulfamic acid and ascorbic acid [Maxwell 2009, Maxwell 2010] and mixture of $Fe(NO_3)_3$, sulfamic acid and ascorbic acid [Egorov 2001, Maxwell 2010b, Maxwell 2011].

For extraction chromatography (and also for ion exchange) Pu is usually desired to be adjusted to +IV which is an intermediate oxidation state. Therefore this is a difficult task. The oxidation state of Pu can only be adjusted entirely to +IV if previously Pu(III) is adjusted. [Kim 2007] Perna et al found that there are two redox reagents which are able to adjust Pu to Pu(IV) from trivalent state: $NaNO_2$ and H_2O_2. The procedure employing H_2O_2 is elaborate since the sample has to be brought close to boiling point to perform the oxidation. [Perna 2001]

The separation of Pu in case of extraction chromatography is usually based on selective oxidation state adjustment. Two solutions are used mainly in the literature. (1) Plutonium is adjusted to Pu(III) and loaded onto TRU column. Prior to Am elution, Pu is adjusted on-column to Pu(IV), finally, Pu is reduced to Pu(III) again to elute it from the column or complexant is used for this reason. [Egorov 2001, Grate 1998, Grate 1999, Eikenberg 2009, Mellado 2002, Pilviö 1998, Thakkar 2002] This solution is used only in case of one extraction chromatographic resin (TRU) since it can retain the trivalent actinides. (2) According to the second solution the oxidation state of Pu is adjusted to Pu(III) then oxidized to Pu(IV) in the load solution. After the sample is loaded onto an extraction chromatographic column, the Pu is reduced to Pu(III) to elute it from the column. [Horwitz 1993, Maxwell 2009, Maxwell 2010, Maxwell 2010b, Maxwell 2011, Vajda 2009, Harrison 2010]

Since +V is the most stable oxidation state of Np in aqueous solution [Radchem Np] and it is not retained on any extraction chromatographic resin, its oxidation state has to be changed prior to loading the sample onto the column. Neptunium can be turned to Np(VI) with a strong oxidizing agent. Osváth et al proved that Np can be oxidized to Np(VI) with $(NH_4)_2S_2O_8$ without $AgNO_3$ catalyst [Osváth 2009]. Neptunium can also be oxidized to Np(VI) with $KMnO_4$ [La Rosa 2008], silver oxide in 0.6 mol L^{-1} HNO_3 [Perna 2002] or BrO_3^- [Ramebäck 1998]. If tetravalent Np was adjusted in the load solution, the oxidation state of Np can change depending on the circumstances of the method: Horwitz et al observed in their studies that if they modified their procedures (elimination of using hydroquinone) some of the Np appeared as Np(VI) while in the presence of the reducing agent all of them were Np(IV). [Horwitz 1993]

In most studies, especially if Pu and Np are separated simultaneously, a strong reducing agent is used that adjusts Np to Np(IV) while Pu to Pu(III). Since in aqueous solutions trivalent Np does not exist, Np(IV) can be adjusted with any strong reducing agent what can be used to adjust Pu(III).

If the sequential separation of many actinides is desired, the oxidation state of them has to be adjusted simultaneously which is particularly elaborate. Plutonium-IV has to be adjusted while Np stays in the form of Np(IV) and U is not reduced to U(V). The conventional procedure in this case is to reduce Pu to Pu(III) and Np to Np(IV) with a strong reducing agent mentioned above. Uranium is present in U(IV) and U(VI), as well [Egorov 2001]. The addition of $NaNO_2$ can turn Pu to Pu(IV) while Np stays Np(IV) because the oxidation of Np is not changed in short time interval, at room temperature [Maxwell 2010b, Maxwell 2011]. Perna et al showed that 25 minutes after the addition of $NaNO_2$ Np(V) appears in the sample if the pre-reducing step was done with Mohr's salt [Perna 2001]. According to Chen et al the presence of Fe^{3+} / Fe^{2+} in the solution behaves as a stability reagent to protect Np(IV) from being reduced to Np(III) or oxidized to Np(V) or Np(VI) [Chen 2001]. The behavior of $NaNO_2$ depends on the conditions of the experiment. E.g. tetravalent Pu and hexavalent Np can be adjusted simultaneously with $NaNO_2$ in 8 mol L^{-1} HNO_3 but in 9 mol L^{-1} HCl / 0.1 mol L^{-1} HNO_3 Pu and Np are tetravalent [Lee M.H. 2007].

The adjustment of odd oxidation states (+III, +V) of Np can be rarely found in the literature. The oxidation state of Np can be adjusted to +III in aqueous solution according to Chen et al. In their experiment Np(III) was adjusted with SO_3^{2-} or $S_2O_5^{2-}$ in low acidity (0.5 mol L^{-1} HCl), O_2-free solutions. [Chen 2001] Ramebäck et al were able to reduce Np to Np(V) using NH_2OH in 1 mol L^{-1} HNO_3 after the oxidation state of Np was adjusted to +VI

using BrO_3^- in their separation procedure based on extraction with HDEHP (di-(2-ethylhexyl)-phosphoric acid) [Ramebäck 1998].

Studies in the literature did not mention often the oxidation state adjustment of U since the most stable oxidation state of it is +VI. It can be easily adjusted to U(IV) with strong reducing agents. Both oxidation states can be retained on the UTEVA and TRU extraction chromatographic resins. If the Pu and the Np are tetravalent after pre-reduction (adjusting Pu(III) and Np(IV)) and $NaNO_2$ addition (adjusting Pu(IV)), the U is assumed to be hexavalent since in the procedures where oxalic acid was used to elute tetravalent actinides the fraction was free from U since preferential complexation of the tetravalent state with oxalic acid complexant occurs [Horwitz 1993, Egorov 2001, Grate 1999]. According to Grate et al the sample treatment used in their experiments ($Fe(NO_3)_3$, sulfamic and ascorbic acid) to reduce the oxidation states of the actinides resulted in the followings: Pu, Am and Cm were trivalent, Th and Np were tetravalent and U was hexavalent [Grate 1999].

2.3. Bulk analysis of actinides

2.3.1. Methods for the separation of actinides

The traditional separation methods for actinides are precipitation, ion exchange, ion exchange chromatography and solvent extraction. The extraction chromatography became widely used in laboratories since a set of extraction chromatographic resins were developed by Horwitz and co-workers and commercialized by Eichrom Inc. (Darien, Illinois, USA) in the early 90's. These five methods are discussed below.

2.3.1.1. Precipitation, coprecipitation

Precipitation is the oldest method for radiochemical separations. Marie Currie used this method first to separate radium and polonium from pitchblende. In the early times the separation methods developed for the isolation of new radionuclides and production of nuclear weapons were, mostly based on precipitation.

In radiochemistry the amount of the measured radionuclide is usually chemically very small to form precipitate or enough precipitate. Carriers (stable isotope of the given radionuclide) in the same chemical form are frequently used in macroscopic quantities to ensure the solubility limit is achieved and the formed precipitate can be practically handled.

Coprecipitation can be applied for those radionuclides for which a suitable isotopic carrier is not available. The radionuclides replace the carrier atoms in the crystal lattice of the

precipitate according to the following three mechanisms. The replacement can be either (1) homogenously distributed (e.g. in case of ^{226}Ra separation with $BaSO_4$) or (2) not isomorphic (e.g. in case of coprecipitation of tri- and tetravalent actinides with lanthanide fluorides (e.g. NdF_3, CeF_3 or with CaF_2). The third mechanism is adsorption. During this process the radionuclides absorb on the surface of the carrier compound. Multivalent metal hydroxides (e.g. $Fe(OH)_3$) and hydrous oxides (e.g. $MnO_2 \times H_2O$) can coprecipitate metals effectively due to generated O^- groups on their surface in neutral and basic solutions. The latter mechanism is less selective than the previous two.

The separation method of precipitation is mainly used for (1) the preconcentration of actinides (using e.g. $Fe(OH)_3$ CaF_2 ...) due to poorer selectivity, (2) the removal of the matrix components and (3) counting source preparation (e.g., by micro-coprecipitation). It can also be used for (4) radionuclide-specific precipitations and (5) the determination of the oxidation states of actinides. [Lehto 2011, Loveland 2006]

2.3.1.2. Ion exchange

Ion exchange is a common method for the separation of radionuclides. Although there are inorganic ion exchangers (e.g. zeolite, bentonite), mostly organic cation and anion exchangers are used. The functional group of the cation exchanger can be, e.g., sulfonate acid ($–SO_3^-H^+$) or carboxylate group ($–CO_2^-H^+$) and that of anion exchanger can be, e.g., quaternary ammonium ion ($–N(CH_3)_3^+OH^-$). Anion exchangers are much commonly used than cation exchangers in actinide separation. Actinides form anionic complexes (most often nitrate and chloride complexes) in strong acids and these are retained on the anion exchanger according to their charge.

The selectivity of an ion exchanger can be characterized by its distribution coefficient (D) which is the ratio of the concentration of an ion in the ion exchanger ($[M]_S$) and its concentration in the solution ($[M]_L$) at the equilibrium state:

$$D = \frac{[M]_S}{[M]_L} \quad (\text{mL/g}^{-1}). \qquad (1)$$

The distribution coefficient at trace level does not depend on the concentration of the given ion therefore the coefficient can be used as a separation parameter for a certain ion. The coefficient depends also on the concentration of other ions with the same charge in the solution, the pH, the size and the charge of the ion, the material of the ion exchanger and the concentration of the media. Saito N. [Saito 1984] collected the distribution coefficients for

selected Dowex resins and showed several methods of the ion exchange separation of certain radionuclides.

For the separation of radionuclides, the ion exchange resin beads are packed into chromatographic columns (ion exchange chromatography) and conditioned with nitrate or hydrochloride acid with the same concentration as the sample solution. Afterwards the sample is loaded onto the column and washed further to remove non-sorbing nuclides. The retained actinides can be separated from each other and other retained elements according to their different sorption strength using usually dilute acids (it can contain redox reagents, as well) or complexing agents.

The ion exchange chromatography does not require carrier like the precipitation methods and the separation performance is also typically better. Anion exchange chromatography has been conventionally used for the separation of Pu, Th or U. [Lehto 2011]

2.3.1.3. Liquid-liquid extraction (solvent extraction)

In case of liquid-liquid extraction the separation of given species takes place by the transfer between two immiscible liquid phases. In the analysis of actinides, the metal species present in aqueous phase are extracted into organic phase while matrix and/or interfering components remain in the aqueous phase. Afterwards the radionuclide is back-extracted from the organic phase. This step can be repeated several times to purify further the investigated actinide.

Three types of extractants can be distinguished: (1) Neutral organic extractants form neutral (ion association) complexes with the actinide ions and the counterions (often nitrates or chlorides). The chemical bonds are formed by electron donor atoms of the organic molecules (oxygen, phosphoryloxygen, sulfur, nitrogen). (2) Amine extractants are complexes of organic cations containing long-chain alkyl or aryl quaternary amines or primary, secondary, tertiary amines and anions. The anions in the complexes can be replaced by anionic actinide complexes. This process is analogous to anion exchange. (3) Acidic extractants are chelates that form complexes with the actinide cations replacing the H^+ in the organic compound. [Vajda 2011]

Solvent extraction is mainly used for the separation of actinides from alkali and alkaline earth metals. Choosing specific extraction reagent and appropriate parameters, metal species can be separated from each other. There are several extraction agents available: e.g. bis(2-ethylhexyl) phosphoric acid (HDEHP) as a chelate can effectively extract trivalent actinide cations besides lanthanides, Fe(III) and Y(III); tenoyltrifluoroacetone (TTA) is a chelate that

can extract only tetravalent actinides at pH 1, but at pH 4-5 it also extracts tri- and hexavalent actinides; tri-butylphosphate (TBP) is a neutral extractant that can extract tetra- and hexavalent actinides. This extractant is used for the separation of U and Pu from spent nuclear fuel in the PUREX process. Tri-octylamin (TOA) is a liquid anion exchanger that is used for the separation of Pu from concentrated nitric acid solution. [Lehto 2011, Loveland 2006, Vajda 2011]

2.3.1.4. Extraction chromatography

Extraction chromatography is the combination of liquid-liquid extraction and column chromatography. The basic separation process is solvent extraction, where the reagent is sorbed on an inert support that can be porous silica or organic polymer forming beads and functions as stationary phase. The mobile phase which is an aqueous solution (most often nitric or hydrochloric acid) passes through the column composed of the beads (so called extraction chromatographic resin). During this process a nuclide in the mobile phase can either be transferred to the stationary phase (retained on the column) or can leave the column without retention. The retained nuclides can be then eluted by changing the eluent composition (acid type and/or concentration), by adjusting the oxidation states of the selected nuclides or using complexing agents. [Braun 1975, Lehto 2011, Horwitz Eichr]

Extraction chromatography due to the extensive contact surface between the two phases, is faster, more efficient and therefore more economic than not only the solvent extraction but also the ion exchange separation method. [Lehto 2011]

There are several extraction chromatographic resins commercially available. Table 4 lists the resins frequently used for actinide separation.

Table 4 Extraction chromatographic resins produced by Eichrom Technologies and Triskem International [Lehto 2011]

Resin	Use	Active component	Separation process
Diphonix® Resin	actinides, transition metals	diphosphoric acid and sulfonic acid	ion exchange
Actinide Resin	group actinide separation	DIPEX	extraction
DGA Resin	actinides, lanthanides, Sr, Y, Ra	N,N,N',N'-tetra-n-octyldiglycolamide	extraction
TEVA® Resin	Tc, Th, Np, Pu, lanthanides	aliphatic quaternary amine	extraction / ion exchange
UTEVA® Resin	Th, U, Np, Pu	diamyl amylphosphonate	extraction
TRU Resin	Fe, Th, Pa, U, Np, Pu, Am, Cm	tributyl phosphate (TBP), octylphenyl-N,N-diisobutyl carbamoylphosphine oxide (CMPO)	extraction

The extraction chromatographic resins can be characterized by their capacity factor (k`, the number of free column volume to peak maximum (Eq. 2)) in the given media:

$$k' = \frac{A_0 - A_S}{A_S} \frac{V_M}{w} \frac{d_{extr}}{N} \frac{V_S}{V_M} = D_V \frac{V_S}{V_M}, \quad (2)$$

where A_0 and A_S are the initial activity and activity at the equilibrium, respectively, V_M and V_S are the volume of the mobile and the stationary phases, respectively, w is the weight of the resin, d_{extr} is the density of the extraction reagent, N is weight percent of the extraction reagent in the resin and D_V is the volume distribution ratio of the given isotope. [Horwitz Eichr]

Nowadays TEVA®, UTEVA®, TRU and DGA resins are used most often for actinide separation. [Lehto 2011] While TEVA® and UTEVA® resin are dedicated to separate tetravalent and tetra- and hexavalent actinides, respectively, TRU resin is not only capable of separating trivalent actinides, but also the capacity factors for actinides are several orders of magnitude higher than those of the TEVA® and UTEVA®. DGA resin is also capable of separating trivalent actinides besides tetra- and hexavalent ones. Therefore, only TRU and DGA resins were selected for the simultaneous separation of all actinides and the properties of these two resins will be shortly detailed in the followings.

The TRU resin is capable of retaining the tri-, tetra- and hexavalent actinides and separating them from most of the matrix components, such as most alkali (Li, Na, K, Rb, Cs) and alkaline earth metals (Be, Mg, Ca, Sr, Ba), some transition and a few other metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Ru, Rh, Pb, Ag, Cd, Hf, Ta, W, Hg) and the heavy lanthanides (Dy, Ho, Er, Tm, Yb, Lu) while Zr, Bi and the light lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) show relatively strong retention in nitric acid media which is the most common load solution. [Horwitz 1993, Horwitz 1995, Vajda 2009]

The TRU resin shows steadily rising retention of the tri-, tetra- and hexavalent actinides with increasing nitric acid concentration. The capacity factors of actinides on TRU are typically two or three orders of magnitude higher than those of actinides on UTEVA®. The TRU resin is also able to retain trivalent actinides. (Fig. 3a) It is has to be mentioned that Fe(III) has a significant negative effect on Am(III) retention due to its suppressing effect therefore the Fe(III) content of the samples has to be reduced either by removal or by turning it to Fe(II) prior to loading on the column since this effect of Fe(II) is negligible. [Horwitz 1993]

The trivalent actinides cannot be retained on the TRU resin in hydrochloride media. The maximum of the capacity factor of Am(III) is approximately 20 (in 8 mol L^{-1} HCl). The k`

values of the tetravalent actinides fall steeply with decreasing concentration of hydrochloric acid from approximately 7 mol L^{-1}. The k` curve of U(VI) has a maximum at approximately 5 mol L^{-1} and it decreases less steeply with decreasing concentration of hydrochloric acid. (Fig. 3a) [Horwitz 1993]

DGA resin shows significantly higher retention for Am especially in HNO_3 even in 0.1 mol L^{-1} and the k' of Am is higher than 100 in HCl with a concentration higher than 3 mol L^{-1} (Fig. 3b). The DGA resin shows steadily rising retention of Am and U and less steep raise for Pu and Th with increasing nitric acid concentration. The values for U are comparable to those for UTEVA®. The k' values of Pu and Th are somewhat smaller in wide concentration range than in case of TRU but significantly higher than in case of UTEVA®. In contrast to other extraction chromatographic resins Am shows high retention (k' is 100...7000 from 2 to 4 mol L^{-1} HCl concentration) in HCl media, as well. The retention curves also show possible elution of Th, U and Am in diluted HCl (< ~1 mol L^{-1}). The retention for actinides on DGA changes significantly in the presence of various components (e.g. Fe, Ca, I...); e.g. the retention for Am increases with a factor of 600 in the presence of 1000 ppm Fe [Eichrom 2006], while the retention for U decreases significantly in HCl media [Groska 2012].

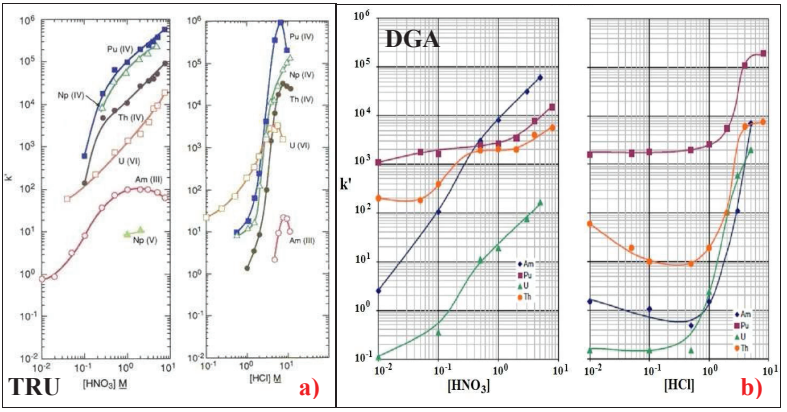

Fig. 3 a) The acid dependency of k' of TRU resin for Th, U, Np, Pu and Am at 23-25 ºC; b) The acid dependency of k' of DGA resin for Th, U, Pu and Am

2.3.2. Literature review on methods for the sequential separation of actinides using extraction chromatographic methods

For the sequential separation of the actinides the combination of two [Eikenberg 2009, Jakopic 2007, Lee M.H. 2007, Mellado 2001, Moody 1998, Pilvio 2000, Thakkar 2002, Varga 2007] or more extraction chromatographic and/or ion exchange columns [Attrep 1992, Maxwell 2006a, Maxwell 2006b, Maxwell 2009, Michel 2008, Pilvio 1998] is the most commonly applied solution in the analysis of different matrices, e.g. water [Maxwell 2006a], soil and sediment [Maxwell 2006b, Eikenberg 2009, Jakopic 2007, Lee M.H. 2007, Mellado 2001, Michel 2008, Varga 2007], urine [Maxwell 2009, Thakkar 2002], radioactive wastes [Lee M.H. 2007] and safeguards swipe samples [Attrep 1992, Godoy 2009] using alpha spectrometry and/or ICP-MS. A single extraction chromatographic column is commonly used for the determination of one (e.g. Pu [Chamizo 2008, Kim 2000, Varga 2007]), two (e.g. Am, Pu: [Grate 1998, Pilvio 2000] or Np, Pu: [Qiao 2010, Rollin 2009]) or sometimes three actinides (e.g. Am, Pu, U: [Berne 1995]; Am, Pu, Np: [Egorov 2001] or Am, Pu, Th: [Gogorova 2007, Olahova 2005, Spry 2000]). Although many radiochemical procedures for the simultaneous separation of actinides based on extraction chromatography have been described in the literature, there are only a few which offer the separation of the major actinides (Th, U, Np, Pu, Am) on a single extraction chromatographic column (Th, U, Np, Pu, Am: Horwitz 1993, Grate 1999, Vajda 2009, U, Np, Pu, Am: Morgenstern 2002, Osvath 2009, Th, U, Np, Pu: Vajda 2003). In the methods of Grate et al [Grate 1999] and Vajda et al [Vajda 2009] either Th and Np or U and Np were eluted together.

The method for the separation of Th, U, Np, Pu and Am proposed by Horwitz et al. [Horwitz 1993] became the base of the determination of all the major actinides on a single column. This procedure is based on selective, on-column oxidation state adjustment of Pu and the use of complexing agents. After the oxidation state adjustment of Pu and Np to tetravalent oxidation state, the samples are loaded in 2 mol L^{-1} HNO_3 onto the TRU column. First Am is eluted with 4 mol L^{-1} HCl then Pu with 4 mol L^{-1} HCl / 0.1 mol L^{-1} hydroquinone to adjust Pu to Pu(III). Thorium is eluted with 1.5 mol L^{-1} HCl prior to Np elution with 1 mol L^{-1} HCl / 0.03 mol L^{-1} oxalic acid and finally U is eluted with 0.1 mol L^{-1} ammonium bioxalate (Fig 4). According to the authors this separation procedure is too tedious for routine analytical application due to the slow kinetics of the tetravalent species. As it can be seen in Fig 4 Th has a very wide elution peak and it can cause the partial co-elution of Np because tetravalent

actinides have not too strong retention in 2 and 1.5 mol L^{-1} HCl. The methods described in the experimental chapters (3.1. and 3.2.) are based on this method.

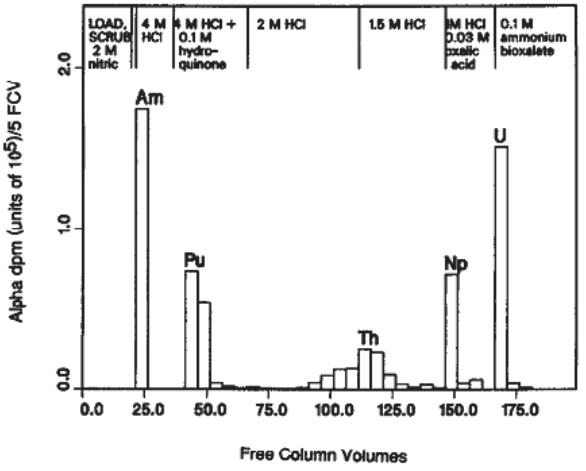

Fig. 4 The sequential elution of five actinides according to Horwitz's method [Horwitz 1993] **(FCV: free column volume)**

Grate et al. [Grate 1999] have published several procedures for the separation of actinides on TRU column. The actinides can be separated in groups according to their valence states in hydrochloric acid media. The trivalent actinides (Pu, Am) are eluted with 4 mol L^{-1} HCl. The elution of the tetravalent actinides (Th, Np) with 1 mol L^{-1} HCl / 0.05 mol L^{-1} oxalic acid is based on the preferential complexation of tetravalent state by oxalic acid compared to that of hexavalent state. The Pu can be selectively eluted if on-column oxidation is taken place using $NaNO_2$ prior to the Am elution and the Pu elution is done by on-column reduction using $TiCl_3$ or the mixture of Fe(II), sulfamic and ascorbic acid in 4 mol L^{-1} HCl. The authors also described a method for the selective separation of Th based on the preferential complexation of Th(IV) by fluoride. Using 4 mol L^{-1} HCl / 0.05 mol L^{-1} HF for the elution of Th resulted in an incomplete separation: the Np and the U could be only eluted together.

In the method of Maxwell S. L. [Maxwell 2006a] three extraction chromatographic columns (TEVA, TRU and SR) are used for the separation of Th, U, Np, Pu, Am and Sr in water samples. The columns were stacked in the following order: TEVA-TRU-SR and conditioned. The samples were loaded in 3 mol L^{-1} HNO_3 / 1 mol L^{-1} $Al(NO_3)_3$ after the oxidation state adjustment with sulfamic acid, ascorbic acid and $NaNO_2$. After the columns were rinsed with 3 mol L^{-1} HNO_3, the TRU and SR columns were removed. The single TEVA

column was washed with additional 3 mol L^{-1} HNO_3 then the Th was eluted with 9 mol L^{-1} HCl and the column was washed with 3 mol L^{-1} HNO_3 again. Finally, Pu was eluted with 0.1 mol L^{-1} HCl / 0.05 mol L^{-1} HF / 0.03 mol L^{-1} $TiCl_3$. Americium was stripped with 4 mol L^{-1} HCl from the TRU column prior to the U elution with 0.1 mol L^{-1} ammonium bioxalate.

2.3.3. Applied measurement techniques

2.3.3.1. Alpha spectrometry

Although many techniques can detect the alpha radiation (e.g. gas ionization detectors such as ionization chambers and proportional counters, scintillation detectors, liquid scintillation counters, solid state nuclear track detectors, radiography, etc.), in alpha spectrometry for qualitative and quantitative analysis of alpha emitting radionuclides semiconductor detectors have been used mainly due to their high energy resolution. The typical energy resolution (expressed as the full width at half maximum of the peak (FWHM)) of an alpha spectrometer with a passivated ion-implanted planar Si detectors (PIPS) is 20-30 keV.

The alpha radiation due to the absorption in the material of the detector and the air layer between the source and the detector and due to self-absorption in the alpha source can suffer from significant energy loss resulting in poor resolution. This effect can be reduced or eliminated by applying the followings: 1) 'infinitely' thin (< 10 μm) alpha sources have to be prepared from the samples, 2) high vacuum in the alpha chamber has to be assured although this will increase the risk of contamination of the detector due to recoil atoms, 3) the distance between the source and the detector has to be increased although this will reduce the detection efficiency, and 4) the entrance window of the detector has to be thin (<10 μm).

Basic alpha spectrometers consist of a detector placed in a light-tight vacuum chamber, electronics to process the signals, a power supply unit (pre-amplifier, amplifier, analog-digital converter and multichannel analyzer) and a software package to evaluate the alpha spectra.

In alpha spectrometry the key point of the analysis is the alpha source preparation which consists of two basic steps: (1) the separation of the radionuclide to be analyzed from the matrix and disturbing elements by a specific chemical procedure and (2) afterwards the preparation of an 'infinitively' thin alpha source by a procedure: e.g. drop deposition (evaporation), electrodeposition, micro-coprecipitation.

The alpha spectrometric analysis is started with the energy calibration carried out by plotting the known energies of the peaks belonging to highest alpha abundance against the

peak location channel numbers referring to the peak centre position. Two-point calibration is appropriate for routine analysis because the calibration curve is linear. The second step is the efficiency calibration which has to be done in case of each measurement geometry. Since the efficiency in alpha spectrometry is independent from the alpha energy, it is enough to determine it with only one isotope. Time to time the goodness of the system has to be checked. This parameter can be characterized by FWHM.

Prior to the measurement of the sample, the background spectrum has to be determined. Alpha peaks have an asymmetric shape starting from the base line that can be modeled usually by a Gaussian shape on the high energy side and exponential low energy tailing. During the spectrum evaluation, first, the isotopes in the sample are determined according to the energy of the alpha peaks. Secondly the activity of each isotope or the detection limits are calculated after the corrections (e.g. background, low tailing if necessary) using the counting efficiency at the measurement geometry.

[Vajda 2011c, Bódizs 2006, Knoll 1989]

2.3.3.2. Gamma spectrometry

Gamma radiation can be detected by many detectors (e.g. ionization chambers, proportional counters, Geiger-Müller counters, scintillation detectors and semiconductor detectors), however, in gamma spectrometry materials with high atomic number and high density are preferred as detectors: scintillation detectors (e.g. NaI(Tl)) and semiconductor detectors (mainly high purity Ge (HPGe) detectors). The energy of the gamma photons characterizes the emitter isotope (qualitative analysis) and the activity (quantitative analysis) can be determined from the intensity of the detected gamma photons (the number of detected gamma photons in a given time interval). Scintillation detectors can be used only in case of samples not producing too many gamma lines. Germanium detectors have significantly better energy resolution therefore it is appropriate for samples containing a mixture of gamma emitting nuclides. The typical energy resolution (FWHM) of a gamma spectrometer with HPGe detector is 1.8-2.0 keV (at the 1332 keV line of ^{60}Co).

Gamma spectrometers usually consist of a detector (with liquid N_2 cooling in case of semiconductor detectors), high voltage supply unit, electric pulse processing unit (pre- and main amplifiers) to amplify and shape the pulses, analogue-to-digital converter (ADC) to digitalize the pulses, multichannel analyzer (MCA) to transform digital pulses into pulse height spectrum and a computer to visualize the collected spectrum.

In case of gamma spectrometry for the analysis of radionuclides with medium or high gamma energy and high abundance, the sample does not need tedious, time-consuming sample preparation (radiochemical separation, source preparation) prior to measurement, however in case of 'difficult-to-determine' radionuclides (e.g. ^{93m}Nb) sample preparation, even radiochemical separation might be necessary [Osváth 2008].

The gamma spectrometric analysis is started with the energy, the peak shape and the efficiency calibration which are more difficult than in case of alpha spectrometry. The energy calibration curve is not linear but usually quadratic therefore at least 6-8 energy points are needed in the examined energy range. More gamma lines are needed also for the efficiency calibration since the efficiency function is really complex in case of both detector types (scintillation and semiconductor detectors). The calibration curve can be determined by theoretical calculations (e.g. Monte Carlo method), as well using specific software (e.g. Genie-2000 ISOCS/LabSOCS software [Canberra]). The goodness of the gamma spectrometric system is characterized by more parameters than in case of alpha spectrometry: FWHM, peak symmetry. Background measurement also has to be carried out prior to the measurement of the sample.

The structure of the gamma spectrum is more complex than that of the alpha spectrum, since the gamma peak of a given isotope sits on the Compton continuum of other gamma emitter isotopes, besides the full energy peaks other peaks resulting from different interactions (pair production, Compton effect, etc.) are present, and a gamma spectrum can contain numerous gamma peaks therefore gamma spectra are analyzed by spectrum evaluation software (e.g. Genie 2000 [Canberra], GSANAL [Bitt], Maestro [Ortec], MicroSAMPO [Aarnio 1987]). After the radionuclides are identified according to their characteristic gamma energies, the gamma peak areas are determined (corrections can be carried out, e.g.: background, real coincidence, self-absorption and dead time corrections, and corrections for the decay during the measurement in case of radionuclide with short half life). Finally, the activity and the detection limit of the identified radionuclides can be determined.

[Bódizs 2006, Knoll 1989, Vajda 2011c]

2.3.3.3. Liquid scintillation counting

Since during the beta decay the energy splits between the beta particle and antineutrino (neutrino), the beta spectrum is continuous and only the maximum beta energy characterizes the emitter isotope. Therefore beta spectrometry is fundamentally different from alpha and gamma spectrometry.

Beta radiation can be detected by gas ionization detectors (e.g. 4π proportional counter), solid and liquid scintillation counters (LSC) semiconductor detectors (e.g. Si detectors). With the exception of GM counters the techniques are theoretically capable of quantitative and qualitative analysis, but in practice the identification of the beta emitting nuclides is very limited due to the continuous nature (energy distribution) of beta radiation. The best technique for beta spectrum acquisition is LSC.

Liquid scintillation counting is based on converting the beta electrons to photons whose energy and intensity are measured in the spectrometer. The sample in appropriate form (in water or diluted acid) is mixed with so-called scintillation cocktail containing primary and secondary scintillators (to convert the radiation energy to photons and to adjust wave length of them), solvent (to make the scintillators soluble) and emulsifier material. The generated photons are converted to electrons on the photocatode of the photoelectron multiplier (PM) tube and then multiplied. The standard LSC contains two photomultipliers (in coincidence circuit), amplifiers (to amplify and shape the pulses), an ADC, a MCA and a computer with an acquiring and spectrum evaluation software, as well.

The analysis by liquid scintillation counting starts with the determination of the level of quench (photon loss due to the components of the sample which causes modification in the spectrum shape) using an external standard source then the efficiency has to be also determined taking into account the quench level and prior to the samples the background has to measured. The activity of the given isotope can be calculated after quench and background correction. [Bódizs 2006, Knoll 1989]

2.3.3.4. Inductively coupled plasma mass spectrometry

In inorganic mass spectrometry not only the element concentration can be determined even in ultra-trace level (pg/g) but also the isotopic composition of most elements (except H, C, N, O, F, Cl and inert gases), since mass spectrometry differentiates also the isotopes. Inductively coupled mass spectrometry (ICP-MS), accelerator mass spectrometry (AMS), thermal ionization mass spectrometry (TIMS), resonance ionization mass spectrometry (RIMS), secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS) have been widely used for the determination of ultra-low levels of selected radionuclides and the precise determination of isotopic ratios. [Hou 2008, Lehto 2011] The application of these techniques is reviewed by several authors: J. S. Becker, D. Lariviere, Hou X. D., Betti M. [Becker 2003, Lariviere 2006, Hou 2008, Betti 2006]. The major applications and the basics of the ICP-MS will be shortly summarized.

ICP-MS has become the most frequently used mass spectrometric technique in the determination of elemental concentration and isotopic composition in trace and ultra-trace level in environmental, biological, geological and waste samples due to its high sensitivity, low detection limit, the capability of fast analysis and simple sample introduction. ICP-MS has been widely used for the determination of isotopes of Th, U, Pu and ^{79}Se, ^{90}Sr, ^{99}Tc, ^{129}I, ^{135}Cs, ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{231}Pa, ^{237}Np, ^{241}Am, ^{243}Am, and ^{244}Cm in environmental and waste samples [Hou 2008].

Usually aqueous solutions are introduced into the ICP-MS through a nebulizer. Due to the nebulization process aerosol with small drop size (< 5-10 μm) is produced in the spray chamber. A part of the aerosol is vaporized into the torch where the inductively coupled plasma (T = 6-8000 K) is generated. The components of the sample are decomposed, atomized and ionized in the plasma. Mainly (~99%) single charged ions are extracted from the normal pressure ion source into the high-vacuum mass spectrometer through an interface (sample and skimmer cone). After the acceleration and focusing by the ion optics, the ions enter into the mass analyzer which is usually quadrupole, double focusing magnetic sector (in the followings sector field) or time-of-flight analyzer where the ions are separated according to their mass-to-charge ratio (m/z). The first two analyzers are the most commonly used in the analysis of radionuclides. Finally, the number of ions are counted and converted into electrical pulses by the detector (electron multipliers or Faraday cups). Isobaric interferences from atomic (e.g., ^{241}Am for ^{241}Pu at m/z = 241) and molecular ions (e.g., $^{238}U^{1}H^{+}$ for ^{238}Pu at m/z = 238), non-spectral interferences (matrix effect: matrix elements can result changes in the analyte sensitivity) and the instrumental limitation (sample-to-plasma transfer and ionization efficiency, abundance sensitivity (tailing effect), stability and detection limits) have to be followed with attention especially in the analysis at trace and ultra-trace level. [Lehto 2011]

The isotope dilution analysis by ICP-MS is only described really shortly. First of all, the ICP-MS system has to be optimized with respect to e.g. maximum $^{238}U^{+}$ intensity, good precision, minimum UO^{+}/U^{+} ratio and/or minimum UH^{+}/U^{+} ratio. Several parameters (i.e., torch position, gas flow rates, different parameters of the ion lenses to maximize the ion extraction) can be modified to achieve the optimal sensitivity (cps (fg g^{-1})$^{-1}$). After tuning the instrument the mass calibration and the determination of the detector dead time have to be performed or checked. Some parameters have to be set daily, some only weekly or monthly depending on the routine method of the given laboratory. Prior to the measurements the applied method (isotopes to be measured, instrument settings during measurement) and the sequence (the order of the blanks, standards, rinse solutions and samples) have to be designed.

2.3.3.5. Combination of alpha spectrometry and ICP-MS

Alpha spectrometry and ICP-MS can complement each other better than replace each other. There are some radionuclides which can be measured only by one technique thus combining them can extend the number of isotopes determined. There are also some radionuclides which can be measured by both techniques and therefore their results can be compared (e.g. ^{244}Cm, ^{242}Pu and the sum activity of ^{239}Pu and ^{240}Pu, ^{241}Am...) improving the reliability of the obtained results.

Both, alpha spectrometry and ICP-MS require the complete separation of the analytes from the matrix components of the sample and from other actinides. In alpha spectrometry it is necessary in order to obtain 'infinitely' thin alpha sources to achieve acceptable resolution for the alpha spectrum and to remove the elements of the basic spectral interferences (e.g. the ^{241}Am peak overlaps with the ^{238}Pu and the ^{237}Np peak with the ^{234}U and the ^{230}Th peaks). ICP-MS also requires the separation of the actinides and the matrix components to remove spectral and non-spectral interferences and to avoid possible matrix effects (e.g. ^{238}U interferes with the determination of ^{237}Np due to abundance sensitivity). Thus alpha spectrometry and ICP-MS can be combined advantageously, because basically the same pre-concentration and separation methods can be used. After the actinide separation the 'pure' fractions containing theoretically only the analyte can be divided and then these aliquots can be handled separately: sources for alpha spectrometry and ICP-MS can be prepared.

In case of a given isotope, the chosen measurement technique depends on its half life, the type of its radiation, the concentration and its abundance. For very long-lived nuclides (e.g. ^{238}U, ^{2358}U, ^{232}Th), ICP-MS can be considered as the preferred technique, since long-lived nuclides have very low specific activity (high specific mass) which requires a significant amount and very long counting time to achieve measureable count rate for alpha spectrometry. On the other hand, significant mass of the given nuclide can reduce the quality of the alpha spectrum due to the self-absorption caused by the thick alpha source. Although in case of low abundance, significant tailing effect can appear during the ICP-MS measurement which causes difficulties in the determination of the given isotope (e.g. ^{236}U due to the abundance sensitivity and the hydride formation of ^{235}U (^{235}U^{1}H)) [Boulyga 2006] or makes alpha spectrometry the preferred measurement technique (e.g., in case of ^{234}U and ^{230}Th). Alpha spectrometry is also difficult in the analysis of ^{236}U due to the similar alpha energies to those of the ^{235}U. For short-lived nuclides at environmental levels, the only possible technique may be the radiometric method (e.g. alpha spectrometry for ^{228}Th).

Although ^{237}Np can be analyzed by alpha spectrometry but only with some difficulties due to its unusual alpha peak shape due to the unusual decay scheme and its low specific activity therefore ICP-MS is the preferred measurement technique but attention has to be taken to the tailing effect caused by ^{238}U and the lack of a suitable tracer causes a big analytical problem in its measurement by both techniques. The reliability of the results would be increased significantly by combining alpha spectrometry and ICP-MS.

In case of Pu isotopes alpha spectrometry is capable of determining ^{238}Pu while it is not possible with ICP-MS at trace and ultra-trace levels because of the isobaric interference of ^{238}U. For the determination of ^{239}Pu and ^{240}Pu in different sample matrices ICP-MS is preferred, since in conventional alpha spectrometry due to the very close alpha energies (5157 keV and 5168 keV for ^{239}Pu and ^{240}Pu, respectively) the alpha peaks of these isotopes cannot be simply decomposed, however, solutions for alpha peak deconvolution were offered by some authors [Siiskonen 2005, Siiskonen 2011, Srinivasan 2006, Vintró 1996]. It has to be mentioned that the ratio of ^{238}Pu/$^{239+240}$Pu in some cases is more informative than ^{240}Pu/^{239}Pu and the tailing effect of ^{238}U and the polyatomic interference of ^{238}U^{1}H in case of ^{239}Pu analysis by ICP-MS have to be taken also in account especially because of the significantly higher mass concentration (typically 10^{6}-10^{9} times higher) of the U isotopes. Plutonium-241 cannot be measured by alpha spectrometry because it is a soft beta emitter, and ICP-MS is also insufficient in its analysis due to its short half life, especially if the ^{241}Pu/^{239}Pu is low. The activity of ^{241}Pu can be calculated from the activity of ^{241}Am or detected by LSC.

The detection limits in the analysis of ^{241}Am obtained by alpha spectrometry and ICP-MS are comparable (typically ~0.1 mBq) and both techniques require extensive chemical separation to remove radionuclides with similar alpha energies (e.g. ^{210}Po, ^{224}Ra, ^{228}Th, ^{238}Pu) and interfering stable elements (e.g. Ti, Hg, Pb, Bi) besides ^{241}Pu causing isobaric interference in ICP-MS, respectively. At ultra-trace level the result for ^{241}Am obtained by alpha spectrometry is more reliable analytically than that obtained by ICP-MS.

[Lehto 2011, Hou 2008, Lariviere 2006, Becker 2003]

There are numerous studies in the literature which combine the alpha spectrometry and the ICP-MS. Some of them use this combination only for the determination of Pu isotopes [Chamizo 2008, Hrnecek 2005, Varga 2008]. Americium isotopes are also often analyzed besides the Pu isotopes [Boulyga 2003, Varga 2007, Varga 2007b]. In case of these isotopes the combination can be performed relatively easily since the same tracer (^{242}Pu and ^{243}Am) can be used for both techniques.

Methods for the determination of more than two actinides which combine these two techniques also can be found in the literature. Maxwell S. L. et al measured ^{239}Pu, ^{242}Pu, ^{237}Np, ^{243}Am, ^{234}U, ^{235}U and ^{238}U by ICP-MS, while ^{236}Pu, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{243}Am and ^{244}Cm by alpha spectrometry for the rapid determination of actinides in urine [Maxwell 2009]. La Rosa J. et al determined ^{237}Np, ^{239}Pu and ^{240}Pu by ICP-MS and ^{237}Np and ^{241}Am by alpha spectrometry in seawater [La Rosa 2005]. Dai X. et al measured ^{238}U, ^{235}U, ^{234}U, ^{239}Pu, ^{240}Pu, and ^{241}Pu by ICP-MS and ^{241}Am, ^{242}Cm, $^{243/244}$Cm, ^{238}Pu and $^{239/240}$Pu by alpha spectrometry in swipe samples [Dai 2011]. Perna L. et al combined many radiometric and mass spectrometric methods: alpha spectrometry (for the determination of ^{241}Am, ^{238}Pu and $^{239+240}$Pu), gamma spectrometry (for the determination of ^{241}Am and ^{233}Pa (daughter of ^{237}Np)), LSC (for the determination of ^{241}Pu), ICP-MS (for the determination of ^{239}Pu and ^{240}Pu), SIMS (secondary ion mass spectrometry used for mapping) and GD-MS (glow discharge mass spectrometry used for the confirmation of the gamma analysis) [Perna 2005].

2.4. Particle analysis

2.4.1. Introduction

Analysis of single radioactive particles involves many different techniques such as alpha track analysis (ATA), fission track analysis (FTA), optical microscopy, SEM (can be combined with X-ray microscopy analysis (XRMA)), micromanipulation, alpha spectrometry, gamma spectrometry and mass spectrometry (mostly LA-ICP-MS, SIMS and TIMS).

Although many studies exist in the topic on the analysis of single, radioactive particles in the literature, there are only a few on particle analysis for safeguards purposes [Baude, Esaka 2004, Iguchi 2005, Lee C.G. 2006, Lili 2009, Park 2006].

The method for particle analysis can consist of several steps: (1) removal of particles from the original sample holder (if necessary), (2) identification and (3) localization of particles of interest (POI), (4) morphological examination (if necessary) and finally, (5) determination of the composition of the particles by destructive or non-destructive analysis. This basic method can be supplemented by screening procedures (e.g. alpha spectrometry, gamma spectrometry) and micromanipulation using optical or scanning electron microscopy.

The procedure obtaining single particles varies according to the different samples matrices (e.g. swipe samples, soil or water), and the different measurement techniques require different sample set-ups: different sample holders need to be used in case of e.g. LA-ICP-MS or SEM.

In this chapter the basic steps of particle analysis will be discussed by summarizing the studies on this topic available in the recent literature focusing on safeguards related techniques. In case of particle analysis for safeguards purposes the investigated particles originate from swipe samples. The use of solid state nuclear track detectors seems to be the most promising technique for combining the procedures for the identification and the localization of particles of interest (particles containing alpha emitting materials) therefore a short description will be given.

2.4.2. Removal of particles from the original media

In order to analyze individual particles usually a thin layer of material has to be prepared. There are many procedures for the preparation of thin samples from the original media (e.g. water, swipe samples, air filters). The so-called "liquid phase extraction" technique involves several techniques applicable for swipe or water samples, e.g. particle removal from swipes by soaking in ultrasonic bath [Baude, Lili 2009, Stetzer 2004], filtration of liquids with membranes of given pore size [Lee C.G. 2006], centrifugation and droplet by droplet deposition of liquids [Sangély 2009]. Baude S. and Park Y. J. used low temperature ashing of swipe samples in their studies [Baude, Park 2006]. The significance of particle removal from swipe samples or air filters by vacuum-impactor [Esaka 2004, Iguchi 2005, Lee C.G. 2006] is increasing nowadays since this technique can be used in clean laboratories. In the Safeguards Analytical Laboratories of the IAEA also this procedure is applied in the determination of U isotopic composition of particles originating from safeguards swipe samples [Kuno 2008].

The removed particles have to be placed on an appropriate sample holder for further investigations. In the followings, techniques appropriate for localization by nuclear track detectors will be discussed.

The most common technique for "particle transportation" is to transfer the particles in an organic solvent and spread them on a plastic or glass surface forming several μm thick layer. Baude et al transferred the particles into ethanol and added collodium. After the evaporation of the alcohol the collodium formed a thin layer fixing the particles on polycarbonate planchet [Baude]. Esaka et al, Iguchi et al and Lee C. G. et al transferred the particles with a vacuum impactor onto a polycarbonate membrane which was later solved in 1,2-dichloroethane dissolved in dichloromethane. Evaporating the organic solvent formed a polycarbonate layer containing the particles. [Esaka 2004, Iguchi 2005, Lee C.G. 2006, Lee C.G. 2007] The above mentioned techniques are used to remove particles from swipe samples.

Another technique for bigger sample (soil or sediment samples) amount is to make pellets of e.g. the soil samples [Jojo 1995] mixing the samples with methylcellulose powder. Similar procedure was also used by Lee M. H. et al [Lee M.H. 2007b].

In case of applying scanning electron microscopy the use of insulator material (e.g. collodium or polycarbonate) has to be avoided. Eriksson et al, Lind et al and Jiménez-Ramos et al transferred the particles onto an adhesive carbon planchet or carbon tape [Eriksson 2002, Lind 2007, Jiménez-Ramos 2006].

Sometimes there is the need to remove individual particles from the previously prepared thin sample layer to further examine them individually. The so-called micromanipulation technique can be used for this purpose. It can be done using a tiny needle under optical microscope [Admon 2007] and under SEM [Admon 2007, Esaka 2009], as well.

2.4.3. Identification of particles of interest (containing alpha emitting material)

The identification of particles of interest is - in this case - to unambiguously distinguish particles containing alpha emitting materials (which can be the traces of the investigated nuclear activity) from the other radioactive and non-radioactive ones which are usually the majority of the particles in the sample.

There are many identification techniques available in the literature. The use of solid state nuclear track detectors implies also the opportunity of the localization besides the identification. Therefore first, a short description on solid state nuclear track detectors will be given followed a review on the two techniques involving them: fission and alpha track analysis. Finally, the other identification techniques will be also briefly discussed.

2.4.3.1. Solid state nuclear track detectors

Solid state nuclear track detectors (in the followings: nuclear track detectors) are mainly organic polymers which can be used to detect radiation with high ionization efficiency (alpha particles, fission fragments, protons). The concept of track formation still has not been clarified completely. It is assumed that the alpha particle along its path produces nanometer size latent track in the material of the nuclear track detector damaging the long carbon chains of the polymers in case of organic materials. The nanometer size tracks are enhanced by etching in basic solvents (e.g. NaOH, KOH) to be able to examine them under optical microscopes since the undamaged bulk material of the track detector is removed slower than the damaged part at the track. The different etching rates result different track sizes. [Bódizs

2006, Rana 2002] Nuclear track detectors are used mainly in radon measurements and neutron dosimetry but they are also applied in space radiation dosimetry [Pálfalvi 2010] and identification of alpha emitting or fissile material in different sample matrices (e.g. soil [e.g. Lee M.H. 2007b] and sediments [e.g. Vaslova 2008], aerosol samples [e.g. Boulyga 1999], swipe samples [e.g. Esaka 2004] for particle analysis).

2.4.3.1.1. Fission track analysis

In case of particle analysis for safeguards purposes one of the most commonly applied techniques is fission track analysis using nuclear track detectors (CR-39, Makrofol, DOWEX or Lexan type) [Baude, Esaka 2004, Iguchi 2005, Jojo 1995, Lee C.G. 2006, Lee C.G. 2007, Lee M.H. 2005, Lee M.H. 2007b, Lili 2009, Lo 2006, Malenchenko 1995, Park 2006, Stetzer 2004, Vaslova 2004, Vaslova 2004, Zhuk 2008].

The samples attached to the nuclear track detectors are irradiated in nuclear reactors with certain thermal neutron flux (varying between 2.57×10^{14} and 5.00×10^{15} neutron cm^{-2} [references in the previous paragraph]) and the thermal neutrons induce fission in the fissile material of the samples. The fission products produce nanometer size, star shaped fission tracks (Fig. 5) on the surface of nuclear track detector. After the irradiation the nuclear track detectors are detached from the samples and etched in NaOH or KOH at a certain temperature (55-70 °C) for a relatively short time (8-90 min) to enhance the size of the nuclear tracks to be able to examine them with optical microscope.

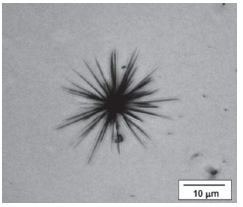

Fig. 5 A typical star shaped fission track [Iguchi 2005]

During the irradiation the material of the track detectors changes significantly due to the high gamma dose in the reactors [Khan 1975, Sharma 1991, Shweikani 1993, Singh 2007]: gamma radiation brakes the long carbon chains and this phenomenon causes opalescence of the nuclear track detectors during even low temperature and short time etching. As an illustration the photos of some nuclear track detectors taken in our laboratory are shown in Fig. 6 to demonstrate this effect: irradiation with a thermal neutron flux of 2.2×10^{12} neutron

cm^{-2} s^{-1} at the Training Reactor of the Institute of Nuclear Techniques and etching with NaOH at 60-70 °C for 8 min (I41947), 26 min (I41966) and 3 min (I41946) resulted remarkable opalescence (Fig. 6 (K90894 is not irradiated and etched)). Opalescence can make impossible the examination by optical microscopes.

Fig. 6 The effect of the irradiation and etching

2.4.3.1.2. Alpha track analysis

Alpha track analysis can be used as an identification technique for alpha emitting nuclides [Bondarenko 1996, Kashkarov 2003, Lee M. H. 2007, Vaslova 2004]. The process of alpha track analysis is similar to the fission track analysis. Instead of the irradiation in nuclear reactors, the nuclear track detectors are exposed to the samples (exposition) for several hours or days depending on the alpha emitting material activity of the samples. During the exposition the alpha particles originating from the sample cause damages in the material of nuclear the track detectors: they form round shaped alpha tracks whose size depends on the alpha energy, the distance of the alpha particle emitting nuclide from the nuclear track detector and the etching parameters (temperature, etching time).

In case of alpha track analysis the used etching parameters are less varied than in case of fission track analysis: the track detectors are typically etched in 6.25 mol dm^{-3} NaOH at approximately 90-95 °C for 4-5 h. Higher etching temperature would cause irreversible changes in the volume of the nuclear track detector (swelling effect) [Sharma 1991, Esaka 2004] which would decrease the precision of the localization of particles.

The observation of the nuclear tracks of alpha particles is significantly easier than that of tracks of fission fragments producing smaller track size. However, the bigger size of alpha tracks decreases the precision of the localization and the time of analysis is also significantly longer than in case of fission track analysis, alpha track analysis does not require irradiation in a nuclear reactor, the samples will not be activated and opalescence will not occur during etching.

2.4.3.2. Other techniques for particle identification

Autoradiography using photographic films can also be used for identification of particle containing alpha and beta emitting nuclides. The degree of blackening is proportional to the activity of the sample. [Kerkápoly 2005] Kerkápoly et al used autoradiography for particle analysis in case of environmental samples, primary coolant samples originating from Nuclear Power Plant, Paks at normal operating conditions and also samples from the spent fuel pond collected after the incident (INES level 3) in 2003. [Kerkápoly 2005, Kerkápoly 2005b, Kerkápoly 2005c]

Jiménez-Ramos et al and Lind et al applied successive splitting of the soil samples looking for 'hot particles' containing ^{241}Am by gamma spectrometry. After the reduction of sample amount, the examination was continued with scanning electron microscopy combined with X-ray microscopy analysis (e.g. energy dispersive X-ray spectrometry (SEM/EDX)). Nuclides with high atomic number can be distinguished from nuclides with low atomic number using this technique due to higher sensitivity for nuclide with higher atomic number. [Jiménez-Ramos 2006, Lind 2007] Eriksson et al combined gamma spectrometry with real-time digital imaging system (IDE Bioscope 3250) and beta camera [Eriksson 2002].

Ketcham et al showed the application of the industrial CT (high resolution X-ray computed tomography) in particle analysis. Gostic et al applied this technique in the identification of weapon-grade Pu particles. [Ketcham 2001, Gostic 2009]

The latter three techniques are not commonly used for the identification of radioactive particles not only because of their high investment and maintaining expenses, but also because of the difficulties of precise localization of the particles of interest.

2.4.4. Localization and relocalization of particles of interest

The studies in the literature only rarely discuss the method of particle localization in detail. Localization using nuclear track detectors (alpha or fission track analysis) is described in more details below.

After the identification of particles containing alpha emitting and/or fissile material using nuclear track detectors, the coordinates of the particles on the sample holder have to be determined according to the coordinates of their nuclear tracks on the nuclear track detector. Moreover, if certain particles are analyzed by different methods using different coordinates systems (e.g. the localization is accomplished in an optical microscope or by SEM and further analysis is executed by LA-ICP-MS), they are needed to be relocated.

Lee C. G. et al placed back the track detectors onto the sample holders followed by etching and placed them under the optical microscope. They determined the coordinates of the nuclear tracks, then the nuclear track detector was removed from the sample, they used these coordinates as the location of the particles. This method had an accuracy of approximately 20 μm and it can be only used in case of really low particle density. [Lee C.G. 2007]

Lee M. H. et al and Vaslova et al applied so called finder grids for the examination by SEM. The grid was coated with boron and during the fission track analysis the fission products and alpha particles originating from the ^{10}B (n,α) ^{7}Li reaction resulted tracks on the surface of the nuclear track detectors. The localization was executed according to the grids on the sample holder and the tracks of grids on the nuclear track detectors. Lee M. H. et al suggested the coating of the grid by U or Th in case of alpha track analysis. This technique has several disadvantages: (1) the tracks originated from the grid can spread widely; (2) in case of high particle density on the sample holder the localization cannot be unambiguous and (3) the grid can cover some particles if it was placed subsequently on the sample holder (Fig. 7). [Lee M.H. 2007b, Vaslova 2004]

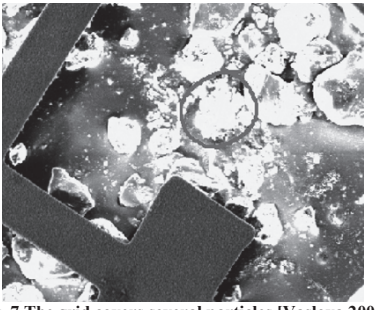

Fig. 7 The grid covers several particles [Vaslova 2004]

More exact procedure is needed for the more precise and unambiguous localization (and relocalization). Admon U. describes calculation methods based on base transformation, namely 2-, 3- and 6-point algorithm [Admon 2007]. These methods use so-called reference points placed on the sample holder and on the nuclear track detector to determine the coordinates of the particles according to the coordinates of their alpha or fission tracks. The reference points define the base vectors of the given base. The coordinates of a nuclear track or a particle can be determined unambiguously in the coordinates system of any microscope (or instrument) using the law of base transformation. These calculation methods result better precision and accuracy of the particle localization than the ones mentioned above. The

mathematical basis of the 3- and the 6-point algorithm will be discussed in detail in chapter 3.4.5.4.1. and 3.4.5.4.2.

2.4.5. Determination of isotopic composition of particles

The isotopic composition of the identified and localized particles can be determined using several techniques. The mass spectrometric methods are most commonly used. At the Safeguards Analytical Laboratories of the IAEA the U and Pu isotopic composition of the radioactive particles originating from swipe samples are analyzed by SIMS. Baude et al, Esaka et al and Lee C. G. et al combined the fission track analysis with TIMS (FT-TIMS). [Baude, Esaka 2004, Lee C.G. 2007]

However, SIMS and FT-TIMS are the most commonly applied measurement techniques in particle analysis, these facilities are not available widespread due to their high investment expenses. Scanning electron microscopy combined with X-ray microscopy analysis is also a widespread technique applied not only for morphological studies but for the determination of the elemental composition. [Jiménez-Ramos 2006, Lind 2007]. Jiménez-Ramos et al applied micro X-ray spectrometry for the detection of the presence of U and Pu in previously localized particles [Jiménez-Ramos 2006].

Boulyga et al first identified localized radioactive particles then separated Pu using a radiochemical method. The Pu isotope ratios were determined by alpha spectrometry or resonance ionization mass spectrometry (RIMS) [Boulyga 1997]. Pöllänen et al used several destructive (SIMS, LSC, ICP-MS and alpha spectrometry) and non-destructive (gamma spectrometry, SEM/EDX) methods besides direct alpha spectrometry [Pöllänen 2007, Ranebo 2010]. The presence of ^{241}Am and $^{239+240}$Pu was detected. [Pöllänen 2006, Pöllänen 2007]

The application of LA-ICP-MS is not widespread in particle analysis. [Admon 2007, Varga 2008b] This technique is so-called quasi non-destructive, since the UV laser ablates only ng amount of the sample surface. This ablated sample part is introduced into the ICP-MS by argon gas flow. In the inductively coupled plasma, the sample evaporates, atomizes and ionizes and these ions are separated and detected in the mass spectrometer. During the examination, the diameter and the energy flux of the focused laser beam is set to the particle size to ablate a part of the particle and the intensities of the U isotopes are registered with ICP-MS [Admon 2007, Varga 2008b]. Although quantitative analysis cannot be accomplished by LA-ICP-MS in the lack of usable, matrix matched standards, it has many promising parameters. The laser beam can be focused well, even to 10 μm and the track of the laser beam on the sample surface can be compared to the diameter of the beam. [Admon 2007] The

particle analysis for safeguards purposes aims to detect the presence of nuclear material and to determine the origin of particles according to their isotopic composition, so the determination of the amount of the U in the particle is not a major requirement.

3. Experimental

3.1. Adaptation of a radioanalytical method for the determination of actinides (Th, U, Pu, Am(Cm)) in safeguards swipe samples

3.1.1. The objectives of the study

The objectives of this study were (1) to adapt a radioanalytical method that was originally developed for the simultaneous determination of Th, U, Pu and Am in small environmental samples for the analysis of swipe samples for national safeguards purposes, (2) to determine the performance parameters of the adapted method by the analysis of blank swipe samples and (3) to demonstrate the performance of this method by the analysis of real samples originating from Hungarian nuclear facilities.

3.1.2. Equipment

The alpha spectrometric measurements were carried out using an alpha spectrometric system containing PIPS detectors (Canberra Inc., USA, Ortec, USA) with different active surface areas (300, 450 and 600 mm^2) and with 48, 37 and 27 keV FWHM, respectively. Detectors were attached to alpha spectrometers (EG&G Ortec, USA, Canberra Inc., USA) and a vacuum system assured the appropriate vacuum (1-100 mbar) in the chambers. The detector backgrounds varied between 0.007 and 0.0008 cps in the range of relevant alpha particle energies from 4 MeV to 10 MeV. The efficiency of the detectors were 12%, 24% and 31%, respectively in the geometry of the measurements (using the detectors of 300, 450 and 600 mm^2, respectively. Counting time varied typically between 30.000 s and 1 day.

3.1.3. Reagents and materials

The used extraction chromatographic resin was TRU (TRISKEM International SAS, 100-150 μm particle size, active component: octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide dissolved in tri-n-butyl phosphate).

All reagents used (Mohr's salt, $NaNO_2$, $TiCl_3$, $TiCl_4$, HNO_3, HCl, HF) were of analytical grade. For dilution distilled water was used. For the experiments ^{243}Am, ^{242}Pu, and $^{232}U/^{228}Th$ were used as tracers. For alpha source preparation 0.2 μm pore size PTFE membrane (Millipore, USA) was used after wetting with ethyl alcohol.

3.1.4. Samples

Blank and real swipe samples were analyzed in order to test the adopted method and to determine its performance parameters (typical recoveries, detection limit (LD)). . Blank samples were clean swipes spiked with radioactive tracers (^{243}Am, ^{242}Pu and ^{232}U/^{228}Th). Real samples were taken by the standard swipe sampling method of IAEA at two locations of the radiochemical laboratory of site 1 where traces of actinides were predicted with significant probability: (1) a laboratory desk (~100 cm^2 sampling area) where samples containing kBq of activities of actinides had been treated (Site #1 Sample #1); (2) the inside surface of a cleaned glass beaker (~50 cm^2 sampling area) (Site #1 Sample #2) used in the examination of samples originated from the fuel damage accident at Nuclear Power Plant Paks in 2003 [Kerkápoly 2005]. Further real swipe samples were taken in various locations in Hungary during national safeguards inspections in 2008 (*Site #1*: an institute operating a training reactor, *Site #2*: a radiochemical laboratory using nuclear material, *Site #3*: a facility producing radioactive isotopes and *Site #4*: a company producing yellow cake).

3.1.5. The original radioanalytical procedure

In this chapter the procedure of Vajda et al [Vajda 2009] for the analysis of Th, U, Np, Am and Pu will be detailed. This procedure was adapted for the analysis of safeguards swipe samples (chapter 3.1.), afterwards it was further improved by extending it for the separation of Np and optimizing for the mutual separation of Np, Th and U (chapter 3.2.).

The original procedure (Fig. 8) was developed for the rapid determination of Am, Pu, Th and U radionuclides in soil and sediment samples for environmental monitoring in emergency situations. The method is based on the fast and complete destruction of small amounts (up to 1 g) of soil or sediment samples by Li metaborate fusion, followed by preconcentration of the actinides by co-precipitation with CaF_2 in acidic media. The precipitate is dissolved in 2 mol L^{-1} HNO_3 containing H_3BO_3 and the tetravalent oxidation state of Pu and Np is adjusted with $NaNO_2$ following the pre-reduction with Mohr's salt. The oxidation states of Am, Th and U are tri-, tetra and most likely hexavalent, respectively. Afterwards the sample solutions are loaded onto a small TRU column (inner diameter: 7 mm; height: 25 mm), Am is stripped with 4 mol L^{-1} HCl, Pu is eluted as trivalent species with 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$ and Th is stripped with 1.5 mol L^{-1} HCl containing $TiCl_4$. Finally, U and Np are eluted together with 0.1 mol L^{-1} HCl / 1.5 mol L^{-1} HF. Alpha sources are prepared from each aliquot directly by

micro-coprecipitation with NdF_3 and the isotopic composition of the alpha sources are calculated by isotope dilution alpha spectrometry. [Vajda 2009]

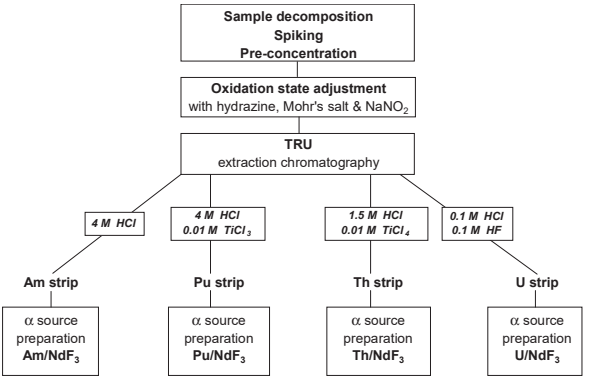

Fig. 8 The flowchart of the analytical procedure

3.1.6. The modifications of the original radioanalytical procedure

The separation procedure based on extraction chromatography and the procedures for alpha source preparation were not modified. The original method - since it was developed for soil and sediment samples - required complete decomposition by fusion and pre-concentration, as well. The method was adapted to swipe samples. This sample - consists of an ultraclean cotton material - is a pure organic matrix that can be easily removed by any dry or wet ashing procedures, therefore the sample decomposition can be simplified compared to fusion and the preconcentration procedure that is responsible for removal of many interfering components can be eliminated. Microwave digestion was chosen as sample destruction followed by multiple evaporation with concentrated HNO_3 and H_2O_2. According to the original procedure, all actinides are reduced during the CaF_2 co-precipitation in the presence of hydrazine, the strong reducing agent. After filtration the excess amount of hydrazine is removed and the tetravalent oxidation states of Pu and Np can be adjusted by the addition of $NaNO_2$. By elimination of the CaF_2 co-precipitation the adjustment of the tetravalent oxidation states of Pu and Np becomes more difficult. Hydrazine had to be used besides Mohr's salt to perform the complete reduction of all actinides and that was checked by rhodanide test. This modification resulted in the presence of hydrazine excess in the load

solution. Therefore the procedure of adjusting Pu(IV) had to be also optimized by using excess amount of $NaNO_2$ compared to the expected amount of hydrazine.

3.1.7. Results of the analysis of blank swipe samples

Blank swipe samples were analyzed to test different sample decomposition methods and to determine the performance parameters of the adapted method.

Two sample decomposition methods were found to be appropriate for swipe samples: microwave digestion and very slow ashing. Acid digestion turned out to be too long and the acid consumption was huge (>300 ml). The ignition of the samples was extremely fast therefore significant loss of actinides was observed.

Since only maximum 0.5 g of organic material can be microwave digested in one PTFE vessel, the swipes had to be divided into four parts using scissors. The process of microwave digestion was based on the method of the Environmental Protection Agency (EPA Method 3052 [EPA 3052]): Ten mL of concentrated HNO_3 were added into the vessels and the temperature of the samples was raised to approximately 180 ºC in 6 minutes and kept at that temperature for 10 minutes. Afterwards the samples were transferred into glass beakers and further destructed by multiple evaporation with concentrated HNO_3 and H_2O_2. The vessels were cleaned first with concentrated HCl and then with concentrated HNO_3 using the same procedure.

The ashing of the swipe samples had to be performed really slowly to avoid ignition of the sample and too extensive fume formation: The temperature was raised by 100 ºC steps and kept in each step for 2-3 hours until 600 ºC was reached which temperature was kept for 6 hours. Afterwards the completely ashed samples were transferred into glass beakers and further destructed by multiple evaporation with concentrated HNO_3 and H_2O_2. Using this procedure no losses of actinides could be observed.

Finally, microwave digestion was selected as the basic procedure to decompose the swipe matrix because it could be performed in significantly shorter time period and less concentrated HNO_3 and H_2O_2 were used during the further acid fuming. Moreover U contamination - originating from the ceramic beakers- were possible in case of ashing.

After the sample decomposition, tracers (^{243}Am, ^{242}Pu, and $^{232}U/^{228}Th$) were added. The tetravalent oxidation states of Pu and Np were adjusted in two steps. Hydrazine was added in 100 µl steps to reduce Fe(III) to Fe(II) as well as Pu to Pu(III), and Np to Np(IV). The lack of Fe(III) was checked by rhodanide test after addition of 100 µl hydrazine followed by 30-

minute heating. Then $NaNO_2$ was added to the cold sample in excess to the hydrazine. The actinides were separated by the extraction chromatographic procedure. Finally, alpha sources were prepared by micro-coprecipitation and analyzed by alpha spectrometry.

After the method for sample decomposition was chosen the performance parameters were determined. The detection limits of several actinides were determined according to the Currie method [Currie 1968] at 95% confidence interval:

$$LD = \frac{2.71 + 3.29\sqrt{N_{bkg}\frac{t_{meas}}{t_{bkg}}}}{\eta \cdot R \cdot t_{meas}}, \qquad (3)$$

where N_{bkg} is the count in the background spectrum at the region-of-interest (ROI) of the given isotope; t_{meas}, t_{bkg} are the measurement time of the sample and the background measurement, respectively; η is the detector efficiency in the geometry of the measurement and R is the chemical recovery.

The detection limits depended mostly on the measurement time and the contamination level of the alpha spectrometric chambers and the PIPS detectors. Table 5 shows three examples of the determined detection limits. The values varied between 0.2 and 7.2 mBq/sample. The detection limits of the Th isotopes were relatively high due to the short measurement time (to avoid the decontamination of the detectors originating from recoiling ions). In case of all the other isotopes the detection limits were bellow 1.5 mBq/sample except one case (Blank #3, ^{241}Am: LD = 2.2 mBq/sample).

Table 5 Detection limits determined by the analysis of blank samples

Isotopes	Detection limits [mBq/swipe]		
	Blank #1	Blank #2	Blank #3
^{241}Am	1.0	1.0	2.2
^{238}Pu	1.5	0.7	0.3
^{239,240}Pu	1.0	0.6	0.2
^{230}Th	4.5	3.2	1.9
^{232}Th	7.2	0.8	3.7
^{233}U	0.8	1.1	0.5
^{234}U	0.8	1.1	0.5
^{238}U	1.0	0.9	0.8

The measurement times (life time) varied between 20 000 and 150 000 s.

Chemical recovery shows the loss of the given actinide during the chemical treatment. In case of complex radioanalytical procedures recoveries higher than 50% can be regarded as good. The recoveries of all the examined actinides (Table 6) were determined for 15 blank samples to check the reproducibility of the method.

Table 6 Chemical recoveries

Sample code	Recoveries			
	Am	Pu	Th	U
#4	80%	58%	52%	73%
#5	67%	n.d.	42%	68%
#6	80%	60%	71%	81%
#7	84%	67%	35%	73%
#8	81%	77%	53%	79%
#9	76%	71%	30%	71%
#10	77%	74%	31%	78%
#11	85%	77%	59%	76%
#12	75%	72%	70%	70%
#13	76%	71%	30%	71%
#14	77%	74%	33%	78%
#15	76%	77%	64%	83%
#16	74%	39%	51%	71%
#17	69%	50%	67%	53%
#18	78%	76%	71%	66%
Average	**77%**	**67%**	**51%**	**73%**
Standard deviation	**5%**	**12%**	**16%**	**7%**

n.d.: not determined

The recoveries of Am, Pu and U were relatively high (77%, 67% and 73%, respectively) and showed acceptable reproducibility. Recoveries for Pu were somewhat lower than the values obtained in the original procedure for soil and sediment samples probably due to incomplete oxidation state adjustment (see above the role of hydrazine). In case of Th the achieved recoveries were usually poor (typically less than 60%) and varied in a wide range (between 30% and 71%). The reason of the high variety was that a part of the Th appeared in the U fraction (Fig. 9) causing significant loss in the Th fraction (therefore poor recovery). The 'Th contamination' in the U fraction caused further problems in the spectrum evaluation. The alpha peak of ^{228}Th overlapped with the alpha peak of ^{232}U and mathematical decomposition of the alpha peaks was necessary; thus the reliability of the calculated recoveries of U decreased. The other fractions (Am, Pu and Th) were free from 'contamination', so the separation can be regarded as good.

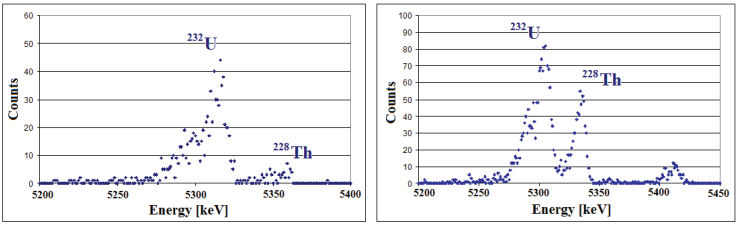

Fig. 9 The alpha spectra of U fractions with different levels of Th contamination

These results showed that the U and Th separation needs to be further investigated. The details can be found in the next chapter.

3.1.8. Results of the examination of the real samples

Real swipe samples were analyzed to demonstrate the applicability of the adapted method for safeguards inspections by detecting actinides in the samples originating from various Hungarian nuclear facilities and determining the isotopic composition of them. The results of the analysis of real samples are summarized in Table 7.

Table 7 The results of the analysis of swipe samples taken at the various nuclear facilities

Isotopes	Activity [mBq/sample]							
	Site 1 #1	Site 1 #2	Site 1 OAH-000/2008-1	Site 1 OAH-000/2008-2	Site 2 OAH-003/2008-1	Site 2 OAH-003/2008-2	Site 4 OAH-001/2008-2	Site 4 OAH-002/2008-1
^{241}Am	-	44.6 ± 1.8	*1.0*	*2.2*	*1.0*	*1.4*	*0.8*	*1.0*
^{244}Cm	-	26.3 ± 1.3	-	-	-	-	-	-
^{238}Pu	-	54.2± 1.4	*0.7*	*0.3*	*1.4*	*1.1*	*0.9*	*1.0*
^{239,240}Pu	-	43.0 ± 1.2	*0.6*	*0.2*	*1.2*	*0.9*	*0.8*	*0.9*
^{230}Th	9.0 ± 1.6	-	*3.2*	*1.9*	*3.1*	*3.8*	*4.7*	*4.5*
^{233}U	10.2 ± 0.7	-	*1.1*	*0.5*	*3.2*	*1.7*	-	-
^{234}U	-	-	-	-	-	-	8.4 ± 0.9	8038 ± 1367
^{238}U	-	-	-	-	-	-	7.4 ± 0.8	8535 ± 1451

Italics: LD; -: LD not determined (see Table 5)

The first two samples (Site #1 Sample #1 and #2) were taken during the method development, the other ones were collected during national safeguards inspections.

Two isotopes, ^{230}Th and ^{233}U were detected in sample #1 taken from the laboratory desk of Site #1 where ^{233}U, ^{230}Th and ^{239}Pu standard tracer solutions of about 100 Bq/ml activity concentrations were treated. In sample #2 taken from the glass beaker (Site #1) ^{241}Am, ^{244}Cm, ^{238}Pu, ^{239}Pu/^{240}Pu were detected, as shown in Table 7. Fuel assemblies had been damaged in an incident in NPP Paks in 2003. After the incident samples from primary coolant were examined at the Radiochemical Laboratory of Site #1. The detected actinides (^{241}Am, ^{242}Cm, ^{244}Cm, ^{239,240}Pu, ^{238}Pu, ^{238}U and ^{234}U) were in 10-15 kBq/l activity concentrations. The elapsed time from the incident was more than ten times of the half life of ^{242}Cm therefore it was not detectable.

The samples of the national safeguards inspections were screened by gamma spectrometry prior to applying the radiochemical method on them. Since high gamma activity was found in the sample taken at Site #4, these samples were not analyzed by alpha spectrometry. Only the screening analysis by gamma spectrometry was evaluated. The following radionuclides were

identified in the gamma spectra: ^{125}I, ^{241}Am, ^{134}Cs, ^{137}Cs, ^{60}Co, ^{153}Sm, ^{152}Eu and ^{154}Eu. These radionuclides are the traces of their activity: production of radiochemicals, radiopharmaceuticals and industrial sources.

In the samples taken in the Radiochemical Laboratory of Site #1 and #2 actinides - above the detection limits - could not be identified. The tables contain only the detection limits. In the samples taken at Site #4 ^{234}U and ^{238}U could be identified which represent their 'nuclear' activity (production of yellow cake). See Table 7.

3.1.9. Conclusions

The radiochemical method [Vajda 2008] was modified by applying microwave digestion as sample decomposition, elimination of the preconcentration and modifying the oxidation state adjustment step. The modified method was successfully adapted for the analysis of safeguards swipe samples and comprehensively tested to determine its performance parameters (detection limits of actinides, typical recoveries, 'goodness' of separation). Real samples were taken during national safeguards inspections of the Hungarian nuclear facilities. The results proved that the modified combined method is relatively fast and simple, it can be effectively used for determination of Am, Pu in swipe samples for safeguards purposes.

The tests discovered an important weakness of the radioanalytical method: the Th and U separation needed to be further optimized. The next chapter will discuss the modification and improvement of the current extraction chromatographic separation technique.

3.2. Method development for the simultaneous determination of actinides (Th, U, Np, Pu and Am(Cm)) using a single TRU column

3.2.1. The objectives of the study

The goal of this study was to develop a radioanalytical method for the simultaneous separation of the major and minor actinides (Th, U, Np, Pu, Am, Cm) on a single TRU extraction chromatographic column based on selective on-column oxidation state adjustment of actinides; and to combine two measurement techniques, i.e. alpha spectrometry and ICP-MS to obtain as much information as possible on the actinide content and actinide ratios of environmental and swipe samples for safeguards analytical purposes.

The procedure of Vajda et al ([Vajda 2009]; see details in chapter 3.1.) was followed without modification till the separation of Am(Cm) and Pu, and the procedure was extended for Np separation, and finally the separation of Th, U and Np was optimized by adjusting the concentration of HCl strip solutions and using Ti^{3+}/Ti^{4+} redox reagents.

First of all, a set of model experiments was performed in order to investigate the oxidation states of U and Np in the load solution of the original procedure (in the media of 2 mol L^{-1} HNO_3) and in the media after the Pu separation step (in 4 M HCl/0.01M $TiCl_3$), See chapter 3.2.5.1.

Our original attempt to strip Np separately from the TRU column, was to adjust the oxidation state of Np to pentavalent which is not retained on TRU column neither in HNO_3 or HCl media. Various redox reagents were tested as candidates for on-column oxidation state adjustment of Np. Modifying the oxidation state of Np would have allowed us to elute Np from the TRU column while Th and U are still retained. See chapter 3.2.5.2.

Previously we found that the addition of Ti(IV) improved the elution of Th (by making the elution profile steeper) and its separation from U/Np. In this study the role of Ti in the Th elution was investigated in more detail. The retention of Ti on the TRU column was determined in HCl media. Furthermore the use of Ti as a potential on-column redox reagent was also examined using Ti(III) and Ti(IV) in the form of TiC_3 and $TiCl_4$, respectively. See chapter 3.2.5.3 and 3.2.5.4.

Then, the separation of Th, U and Np was optimized. See chapter 3.2.5.5.

Finally, the procedures for the preparation of sources for alpha spectrometry and ICP-MS measurements have been elaborated.

Based on the experiences of the model experiments, test, reference swipe and environmental certified reference material (CRM) (IAEA-135) samples were analyzed to characterize (to determine the recoveries and the detection limits) and to validate the improved radioanalytical procedure. See chapter 3.2.7. Reference materials (IAEA-135) were also analyzed for method validation purposes.

3.2.2. Equipment

Alpha sources were counted with an alpha spectrometer (Canberra Inc., USA) equipped with Si semiconductor (PIPS) detector with an active surface area of 450 mm^2. The detector background was less than 0.0001 cps in the 3.5–9 MeV energy range. The efficiency of the detectors was 25% in the geometry of the measurements. Counting time was typically 1 day.

The ICP-MS analysis was carried out using an Element 2 ICP-MS (Thermo Electron Corp., Germany) with magnetic sector field and single electron multiplier. The measurements of model experiments were carried out in low resolution mode using Conical nebulizer (AHF, Germany). A peristaltic pump was used to inject the sample in the Scott type spray chamber (AHF, Germany). The validation was carried out using also an Element 2 ICP-MS in low resolution mode using a high efficiency inlet system, Apex HF (Elemental Scientific, USA) in self-aspirating mode.

The LSC analysis was carried out using a Tri-Carb 2800TR low activity scintillation analyzer (Canberra / Packard (USA)).

The gamma spectrometry measurements were carried out in a gamma spectrometry system built up by either an EGPC 12 type HP Ge (FWHM = 1.70 keV at 1333 keV; relative efficiency: 12.8%) or a coaxial HP Ge detector (FWHM = 1.95 keV at 1333 keV; relative efficiency: 101.2%) and an 8k multichannel analyzer. The gamma spectra were acquired and evaluated with either an Ortec Maestro or a Canberra Genie 2000 gamma analysis software.

3.2.3. Reagents and materials

The used extraction chromatographic resins were TRU (TRISKEM International SAS, 100-150 μm particle size, active component: octylphenyl-N,N-di-isobutyl carbamoylmethylphosphine oxide dissolved in tri-n-butyl phosphate) and DGA (TRISKEM International SAS, 50-100 μm particle size, active component: N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide). The resins were placed in plastic BioRad columns.

In case of the model samples ^{230}Th or ^{232}Th, ^{233}U and ^{237}Np were used as tracers. In case of the test and swipe samples ^{243}Am, ^{242}Pu, ^{229}Th, ^{237}Np and ^{233}U were used as tracers. In case of IAEA-135 reference material ^{243}Am, ^{242}Pu, ^{229}Th, ^{239}Np and ^{233}U were used as tracers.

All reagents used (Mohr's salt, hydrazine, $NaNO_2$, $TiCl_3$, $TiCl_4$, $KMnO_4$, $K_2S_2O_8$, $K_2Cr_2O_7$, $K_2S_2O_5$, Na_2SO_3) were of analytical grade. Acids (HNO_3, HCl, HF,) and H_2O_2 used for ICP-MS analysis were of Suprapur grade (Merck, Darmstadt, Germany and Seastar Chemicals INC, Canada) and for alpha spectrometric and LSC analysis were of analytical grade. For dilution ultrapure water (Milli-Q System, Millipore, USA) was used. For alpha source preparation 0.1 μm pore size cellulose ester membrane (Millipore, USA and Pall, USA) was used. For LSC measurements ProSafe HC LSC cocktail was used.

3.2.4. Samples

Model samples for the model experiments were spiked HCl or HNO_3 acids. The used tracers were the mixture of several actinides as listed above depending on the given experiment. Test, swipe and environmental CRM (IAEA-135) samples were analyzed to test and validate the final analytical procedure. Test samples contained only ^{243}Am, ^{242}Pu, ^{229}Th, ^{237}Np and ^{233}U as tracers in 2 mol L^{-1} HNO_3. Swipe samples were either blank or reference swipe samples of IAEA containing known amounts of U (WIM-5-U) and Pu (NBL CRM 122).

3.2.5. Model experiments

Model experiments were done in order to study chromatographic behavior of Th, U and Np in more details. The Am and Pu separation of our original procedure [Vajda 2009] was not modified.

For each model experiment approximately 1 mL wetted TRU resin was placed in a plastic BioRad column (length: 25 mm, average inner diameter: ~7 mm) and quartz crystals were placed on the top to avoid mixing of the resin. Known amounts of tracers were used. The load solution was always 10 mL 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$ (the term load solution in the model experiments always refers to this condition) to simulate the condition after the Pu separation, because this is the composition of the Pu strip solution according to the original method. Solutions were passed through the TRU column by gravity flow (approximately 1 mL/min). Five mL fractions of the eluates were collected and measured by either ICP-MS or LSC. Approximately 1% of the original load solution was kept and the actinide content of it

was compared to that of each 5 mL fraction. The elution profile of Th, U and Np was determined by ICP-MS. If only the behavior of Th was investigated, LSC measurements were applied using ^{230}Th as tracer to obtain higher accuracy.

3.2.5.1. Oxidation state of Th, U and Np

Since the original goal was to separate Th, U, Np, using selective, on-column oxidation state adjustment, the oxidation states of the given actinides had to be first determined after the Pu elution of the original method [Vajda 2009]; where Pu is stripped from the column with 10 mL 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$. The Ti(III) reduced Pu from Pu(IV) to Pu(III), which is not retained on the TRU column. The oxidation states of Th and Np were presumably tetravalent, the oxidation state of U(IV,VI) was experimentally studied.

First of all, the elution profile of Th, U and Np was investigated using 2.5 mol L^{-1} HCl eluent (Fig. 10) without the presence of any oxidizing or reducing agents. The load solution (10 mL 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$) contained known amounts of ^{232}Th, ^{233}U and ^{237}Np. After loading and washing step (with 5 mL 4 mol L^{-1} HCl) the TRU column was washed with 5 mL fractions of 2.5 mol L^{-1} HCl seven times. Finally, all the still retained actinides were eluted with 20 mL 0.1 mol L^{-1} HCl / 0.1 mol L^{-1} HF. Each fraction was collected separately and measured by ICP-MS.

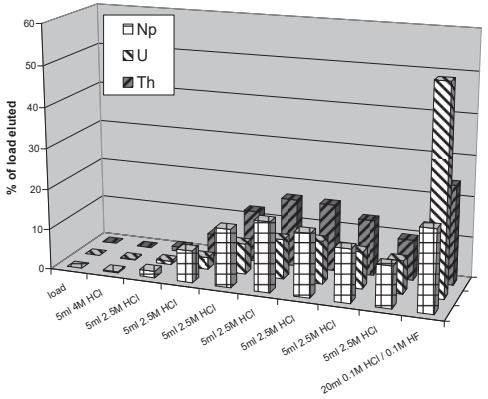

Fig. 10 The elution profile of Np, U and Th obtained by washing the TRU column with 2.5 mol L^{-1} HCl

Thorium, Np and U are not separated and not completely eluted with 2.5 mol L^{-1} HCl. The elution of Th and Np was similar to what could be expected from the values of the capacity factors (k') on TRU in 2.5 mol L^{-1} HCl ([Horwitz 1993]; k'(Th(IV))~40, k'(Np(IV))~600).

The results confirmed that Th and Np were in tetravalent state. The figures of nitric acid and hydrochloric acid dependencies of k' for selected actinides on TRU resin in the paper of Horwitz et al [Horwitz 1993] do not contain information about U(IV) but since the elution profile of U obtained by this experiment was similar to that of Th and Np, a part of U was assumed to be in U(IV) oxidation state, as well.

It could be concluded that the oxidation states of the investigated actinides after the Pu elution step were determined. The oxidation states after the Pu elution are Th(IV), Np(IV) and U is partially U(IV) and U(VI).

3.2.5.2. Attempts to on-column oxidation state adjustment of Np

For the separation of Th, U, Np on a single TRU column, our original objective was to adjust the oxidation state of Np to pentavalent which does not form stable complexes and is not retained on a TRU column either in HNO_3 or in HCl media while Th and U can stay on the TRU column as tetra- or hexavalent species. Neptunium(V) is the most probable oxidation state of Np in aqueous solution [Radchem Np]. We planned to adjust its oxidation state and to elute it with 1 mol L^{-1} HNO_3 or 3 mol L^{-1} HCl then follow the original procedure for the Th and the U elution.

Known amounts of ^{232}Th, ^{233}U and ^{237}Np were loaded in 10 mL 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$ onto the TRU column in 4 mol L^{-1} HNO_3/0.01 mol L^{-1} $TiCl_3$. After loading the column was washed with 5 mL 4 mol L^{-1} HCl to remove excess Ti, then different oxidizing reagents with different concentrations were used: 0.001 mol L^{-1} and 0.05 mol L^{-1} $KMnO_4$, 0.1 mol L^{-1} $NaNO_2$, 0.001 mol L^{-1} and 0.05 mol L^{-1} $K_2S_2O_8$, 0.05 mol L^{-1} $K_2Cr_2O_7$ in 1 mol L^{-1} HNO_3; 0.05 mol L^{-1} $TiCl_4$ in 1.5 mol L^{-1} HCl. Five mL fractions were collected separately and measured by ICP-MS. None of the oxidizing reagents was able to adjust Np to Np(V) on column. Either the Np remained Np(IV) as a result of the reducing power of the resin or it was turned to Np(VI) that is also retained by the resin (see later in chapter 3.2.5.4.).

After the unsuccessful oxidizing I also tried to adjust the oxidation state of Np to Np(III) on the TRU column, since trivalent actinides are not retained on TRU in hydrochloric acid media. According to Chen et al [Chen 2001] Np can be reduced to Np(III) in aqueous solutions. Three reducing reagents were used: 0.05 mol L^{-1} $K_2S_2O_5$ and 0.05 mol L^{-1} $NaSO_3$ in 3 mol L^{-1} O_2 free HCl and 0.05 mol L^{-1} $TiCl_3$ in 1.5 mol L^{-1} HCl. Each 5 mL fraction was collected separately and measured by ICP-MS. None of the reducing reagents were able to adjust Np to Np(III) on column. The Np remained Np(IV).

None of our attempts to adjust Np to either Np(V) or Np(III) on the TRU column was successful showing the difficulty of on-column oxidation state adjustment compared to procedures carried out in aqueous solutions.

3.2.5.3. Role of Ti in Th elution

According to the paper of Vajda et al [Vajda 2009] the addition of Ti(IV) seemed to affect the elution of Th making the elution profile steeper and the separation of Th from U/Np. In this chapter the effect of Ti on the Th elution was investigated in more details. The retention of Ti(III) and Ti(IV) was also determined in 1.5 and 4 mol L^{-1} HCl media.

A known amount of ^{230}Th was loaded in 10 mL 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$ onto the TRU column. The column was washed with 5 mL 4 mol L^{-1} HCl then Th was eluted either with (1) 2.5 mol L^{-1} HCl without the presence of Ti, (2) 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$, or (3) 2.5 mol L^{-1} HCl / $TiCl_4$ (Seven 5 mL fractions were collected indicated as 1-7 in Fig. 11). Finally, all the still remaining Th was eluted with 20 mL 0.1 mol L^{-1} HCl / 0.1 mol L^{-1} HF (fraction 8). Each fraction was collected separately and measured by LSC.

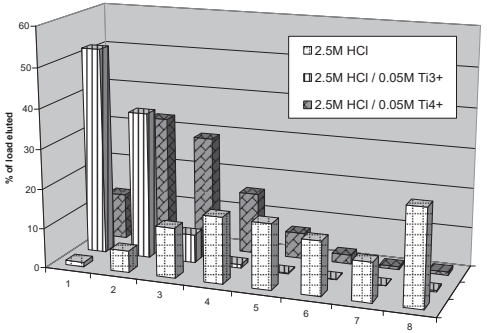

Fig. 11 Elution of Th from TRU column

The results are shown in Fig. 11 The elution profile of Th obtained by pure 2.5 mol L^{-1} HCl was wide and only 75% of the loaded amount could be eluted with 35 mL 2.5 mol L^{-1} HCl. The elution profile was significantly narrower using 0.05 mol L^{-1} $TiCl_3$ or $TiCl_4$ in the eluent, and 100% of the Th could be eluted within 7 fractions. Titanium can be considered as a Th analogue that helps remove Th by co-elution. In case of Ti(III) and Ti(IV) 20 and 30 mL of eluent is needed to elute 100% of Th, respectively. It is not clear why the use of Ti(III) resulted in a slightly narrower elution peak than that of Ti(IV).

The beneficial effect of Ti on the Th elution could be observed only at a relatively high Ti concentration (0.05 mol L^{-1} Ti). Fig. 12 shows – as an example – that Ti^{4+} could probably oxidize Np and U to Np(VI) and U(VI) at 0.01 mol L^{-1} concentration what is revealed in the chromatogram by the strong retention of these species (see in 4.2.5.4.), but it did not help the Th elution. As a comparison see Fig. 11. (Experimental conditions: After loading known amounts of ^{232}Th, ^{233}U and ^{237}Np the TRU column was washed with 5 mL 4 mol L^{-1} HCl, 5 mL 2.5 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_4$ two times, 5 mL 1.5 mol L^{-1} HCl five times and finally with 20 mL 0.1 mol L^{-1} HCl / 0.05 mol L^{-1} HF.) It has to be mentioned that the 0.1 mol L^{-1} HCl / 0.05 mol L^{-1} HF solution containing the strong complexing agent F is able to remove all actinide species from the TRU column, therefore it is added as a final strip solution in all experiments.

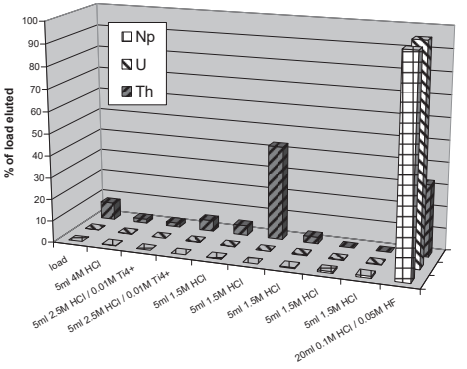

Fig. 12 The 0.01M mol L^{-1} Ti(IV) could adjust the oxidation state of Np and U to hexavalent but it had no effect on the Th elution

The retention of Ti on the resin was also investigated in order to understand the retention mechanism of Ti and Th. Approximately 0.5 mg of Ti(III) and Ti(IV) were loaded onto TRU columns. Then the columns were washed with 5 mL 4 mol L^{-1} and 5 mL 1.5 mol L^{-1} HCl five times each. The fractions were collected separately and the Ti content was measured by ICP-MS. Both Ti species could be eluted with 15 mL 4 mol L^{-1} and with 10 mL 1.5 mol L^{-1} HCl. Slight differences could be observed between the elution profiles of Ti(III) and Ti(IV). It is likely that Ti in both oxidation states is slightly retained on TRU resin with increasing capacity factor at higher HCl concentration. Titanium in both oxidation states and at elevated concentration can replace Th on the resin thus it helps remove it.

3.2.5.4. Titanium as redox reagent

The use of Ti as on-column redox reagent was investigated in more details using Ti(III) and Ti(IV). It is well-known that Ti(III) can reduce U(VI) to U(IV) in dilute HCl [Maxwell 2006a, Maxwell 2006b, Maxwell 2008]; moreover, it can reduce Pu(IV) to Pu(III) on the TRU column [Vajda 2009]. In this study I examined whether Ti(III) is able to reduce Np(VI) to Np(IV) and U(VI) to U(IV) on-column and whether Ti(IV) is able to oxidize Np(IV) to Np(VI) and U(IV) to U(VI) on-column. These model experiments were done in the presence of Th, U and Np to follow their behavior simultaneously.

Known amounts of ^{232}Th, ^{233}U and ^{237}Np were loaded in 10 mL 4 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ onto the TRU column to make sure Np and U are in the hexavalent state. After loading, the column was washed with 10 mL 4 mol L^{-1} HCl to remove Ti(IV) from the TRU column then with 5 mL 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ six times and finally with 20 mL 0.1 mol L^{-1} HCl / 0.1 mol L^{-1} HF (Fig. 12). Each fraction was collected separately and measured by ICP-MS.

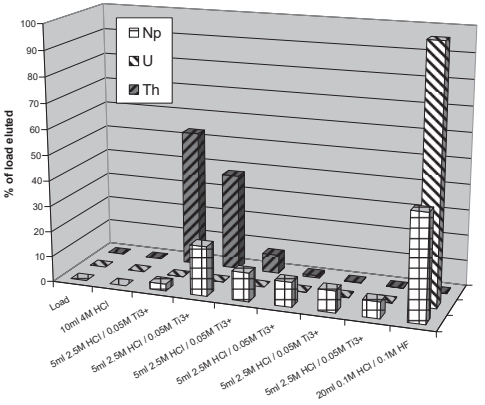

Fig. 13 Elution of Th from the TRU column with 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$

According to the results shown in Fig. 13 Ti(III) could reduce approximately 60% of Np to Np(IV) while U remained hexavalent because about 60% of Np appeared in the 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ fractions and U could only be eluted with the 0.1 mol L^{-1} HCl / 0.1 mol L^{-1} HF.

Known amounts of ^{232}Th, ^{233}U and ^{237}Np were loaded in10 mL 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$ onto the TRU column. After loading, the column was washed first with 10 mL 4 mol L^{-1} HCl to remove most of Ti(III) from the TRU column, secondly with 5 mL 4 mol L^{-1} HCl / 0.006 mol L^{-1} $TiCl_4$, then with 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ six times 5 mL and finally, with 4 mol L^{-1} HCl twice 5 mL (Fig. 14). Each fraction was collected separately and measured by ICP-MS.

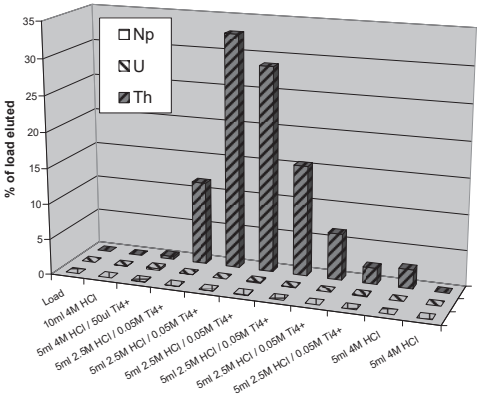

Fig. 14 Elution of Th from the TRU column with 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$

In Fig. 13 the 6 times 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ fractions contained almost 100% of Th but no U and Np. It was assumed that tetravalent actinides can be eluted similarly to Th (see Fig. 11). According to Horwitz et al [Horwitz 1993] the k` value of U(VI) in 2.5 mol L^{-1} HCl is approximately 1000 (which means a relatively strong retention) and U did not appear in the 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ fractions, it can be concluded that the oxidation state of U was U(VI). However, there is no data about Np(VI) in the paper of Horwitz et al [Horwitz 1993], we presumed the curve of k' could be similar to that of U(VI) therefore the oxidation state of Np was assumed to be Np(VI).

It was confirmed that Ti can be used not only as on-column reducing agent because Ti(III) reduced Np(VI) to Np(IV) but also as on-column oxidizing agent because Ti(IV) oxidized Np(IV) to Np(VI) and U(IV) to U(VI). Aware of these results it is also likely that the strong oxidizing agents, e.g. $K_2S_2O_8$, $KMnO_4$ oxidized Np directly to hexavalent state (if kinetic effects are disregarded) and did not allow the stripping of the unstable Np(V) species (see 4.2.5.2.). Titanium(IV) was chosen for Th elution in the optimized procedure. Although, eluting Th in the presence of Ti(IV) a wider Th peak is obtained than in the presence of

Ti(III), but Ti(IV) also oxidizes Np to Np(VI) which is better retained on the TRU column than the reduced Np(IV) resulting in a pure Th fraction.

3.2.5.5. Optimization of Th, U and Np separation

In the previous chapters (3.2.5.3. and 3.2.5.4.) it could be seen that the presence of Ti improved the Th elution. The elution peak of Th became narrower compared to one without using Ti (Fig. 10) and Th could be eluted completely from the TRU column with 2.5 mol L^{-1} HCl (Fig. 11).

The Th elution in the presence of Ti(IV) was tested under different concentrations of HCl. The load solutions (10 mL 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$) containing known amounts of ^{232}Th, ^{233}U and ^{237}Np were loaded then the TRU column was washed first with 10 mL 4 mol L^{-1} HCl to remove the traces of Ti(III) from the TRU column, secondly with 5 mL 4 mol L^{-1} HCl / 0.006 mol L^{-1} $TiCl_4$, then either with (1) 1.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ six times 5 mL and with 20 mL 0.1 mol L^{-1} HCl / 0.1 mol L^{-1} HF (Fig. 15a); (2) 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ six times 5 mL (Fig. 15b) and (3) 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ six times 5 mL (see Fig. 14 above). Finally, the latter two columns were washed with 5 mL 4 mol L^{-1} HCl twice. Each fraction was collected separately and measured by ICP-MS.

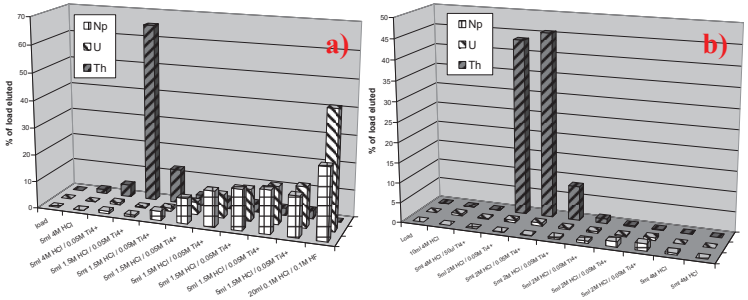

Fig. 15 The elution profile of Np, U and Th obtained by washing the TRU column with a) 1.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ b) 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$

In case of using 1.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ (Fig. 15a), the elution peak of Th was narrow but after 10 mL eluent U and Np started to leak. The use of 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ (Fig. 14) resulted in a wider elution peak for Th, but U and Np were fully retained on the TRU column. Eluting the Th with 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ (Fig. 15b), the obtained elution peak of Th was still narrow; furthermore U and Np were retained on the TRU column.

In the final separation procedure the Th was eluted using 20 mL 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$.

After efficient removal of Th from the TRU column, the separation of Np and U had to be optimized. At this point Np and U on the TRU column were in hexavalent state. Neptunium was planned to be eluted with 0.05 mol L^{-1} $TiCl_3$ as on-column reducing agent in HCl media to selectively set its oxidation state to tetravalent while U remained in hexavalent state. Although Ti(III) can reduce both actinide species on-column, the reduction of Np(VI) to Np(IV) is supposedly faster than that of U(VI) to U(IV). Furthermore the lower the HCl concentration, the faster the elution therefore less time is available for the reduction, however at low HCl concentration the elution of the hexavalent actinides started, as well. Thus optimal HCl concentration had to be found to be able to separate Np from U. The effect of the combinations of tree different concentrations (1.5, 2 and 2.5 mol L^{-1}) of HCl was examined in the presence of 0.05 mol L^{-1} $TiCl_3$ (Fig. 16a-16d).

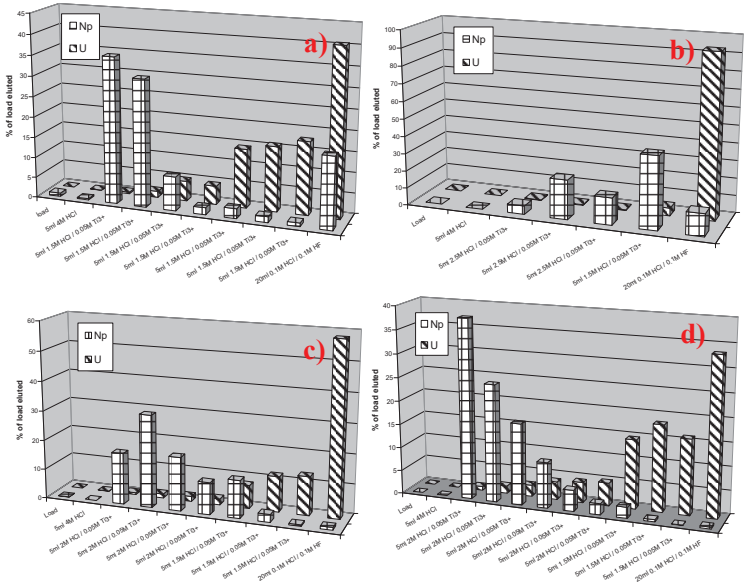

Fig. 16 The elution profile of Np and U obtained by washing the TRU column with a) 1.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$; b) 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ and 1.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$; c) 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ and 1.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$; d) 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ and 1.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ - after loading the first 5 mL of stripping solution the column was closed for 15 minutes

In case of using 1.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ (Fig. 16a) approximately 85% of Np was eluted with 35 mL eluent but this fraction contained approximately 60% of the U, as well. Using 2.5 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ (Fig. 16b) resulted in a very low Np elution: the first 15 mL of the eluate contained only approximately 40% of the Np. Approximately 80% of the Np could be eluted from the TRU column with 20 mL 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$ (Fig. 16c) and only 6% of U appeared in the Np fraction. The reduction of Np to Np(IV) seemed to be slow according to the obtained elution curve, therefore after loading the first 5 mL 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$, the column was closed for 15 minutes to give time for the reduction (Fig. 16d). In this case approximately 90% of the Np could be eluted from the column with 20 mL of the eluent while less than 10% of the U was in the Np fraction.

In the final optimized separation procedure the last elution condition was selected and a washing step with 10 mL 2 mol L^{-1} HCl was fitted between the Np (20 mL 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$) and the U (20 mL 0.1 mol L^{-1} HCl / 0.1 mol L^{-1} HF) strip solutions to make sure that the U fraction contains only traces of Np.

3.2.6. The optimized separation procedure

3.2.6.1. Sample decomposition and pre-concentration of actinides

Samples (e.g. sediment samples) are fused with $LiBO_2$ and actinides are pre-concentrated by co-precipitation with CaF_2 according to the original method [Vajda 2009]. In case of samples with simple matrix such as safeguards swipes the samples are only ashed and no pre-concentration is applied.

3.2.6.2. The extraction chromatographic procedure for the simultaneous determination of Th, U, Np, Pu and Am

After the sample decomposition (without pre-concentration) the samples are taken up in 10 mL 2 mol L^{-1} HNO_3. The desired oxidation states of the actinides are adjusted by adding 50 mg Mohr's salt, approximately 2-300 µl hydrazine and 60 mg $NaNO_2$. When CaF_2 pre-concentration is performed, only $NaNO_2$ is used (to adjust Pu to Pu(IV)) since the pre-concentration is done in reducing media.

The TRU column is conditioned with 10 mL 2 mol L^{-1} HNO_3 and freshly prepared 10 mL 2 mol L^{-1} HNO_3 / 0.1 mol L^{-1} $NaNO_2$. The sample is loaded onto the TRU column then washed with 15 mL 2 mol L^{-1} HNO_3 / 0.1 mol L^{-1} $NaNO_2$ to remove the residual matrix components.

Americium (and Cm) isotopes are eluted from the TRU column with 10 mL 4 mol L^{-1} HCl. The column is washed with 5 mL 4 mol L^{-1} HCl to remove the traces of Am.

Plutonium isotopes are eluted with freshly prepared 10 mL 4 mol L^{-1} HCl / 0.01 mol L^{-1} $TiCl_3$. The Ti(III) is removed from the column with 15 mL 4 mol L^{-1} HCl. Then 5 mL 4 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$ are loaded onto the column.

Thorium isotopes are eluted with 20 mL 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_4$. The Ti(IV) is washed from the column with 15 mL 4 mol L^{-1} HCl.

Neptunium isotopes are eluted with freshly prepared 20 mL 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$. After loading the first 5 mL 2 mol L^{-1} HCl / 0.05 mol L^{-1} $TiCl_3$, the column is closed for 15 minutes to let all the Np(VI) turn to Np(IV). The column is then washed with 10 mL 2 mol L^{-1} HCl to remove Ti(III) and the traces of Np.

Finally, U is eluted with 20 mL 0.1 mol L^{-1} HCl / 0.1 mol L^{-1} HF.

The flow-chart of the procedure is shown in Fig. 17.

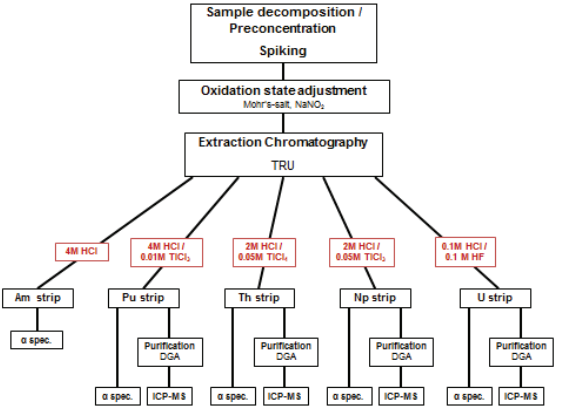

Fig. 17 The flowchart of the analytical procedure

3.2.6.3. Sample dividing and source preparation for alpha spectrometry and ICP-MS

The Am fraction is measured only by alpha spectrometry. The Th, U, Np and Pu fractions were divided into two parts. Typically approximately 90%, 20%, 50% and 50-75% of the Pu, Th, Np and U fractions are used for alpha spectrometry, respectively. The alpha sources are prepared by micro-coprecipitation with NdF_3 according to the method described in detail by

Vajda et al [Vajda 2009]. For the preparation of Pu, Np and U sources strong reducing agents are added to the solutions before precipitation.

Preparation of the sample aliquots for ICP-MS measurements is more delicate and time-consuming than that of the alpha source preparation that is performed in a straight forward way by micro-coprecipitation with NdF_3 from the strip solutions. Prior to the measurement by ICP-MS the salt content (in our case Ti) has to be reduced in the Th, Np and Pu fractions. For purification of the different fractions small DGA columns were used according to Groska [Groska 2012]. Separations on DGA resin had the further advantage that higher decontamination factors were achieved against other actinides (see the complete flow chart in Fig. 16).

Purification of the Np fraction: The Np fraction might contain a detectable amount of U which also has to be eliminated. The U fraction has to be purified from HF. For the purification steps small DGA extraction chromatographic columns (containing 150 mg resin) are used. The concentration of the Np fraction (originally 2 mol L^{-1} HCl) is set to 4 mol L^{-1} HCl with concentrated HCl. A few drops of concentrated HNO_3 are added to turn Ti(III) to Ti(IV). The sample aliquot is loaded onto a DGA column and the column is washed with 5 mL 4 mol L^{-1} HCl, 20 ml 0.1 mol L^{-1} HNO_3 / 0.1 mol L^{-1} $K_2S_2O_8$ and finally 5 ml 0.1 mol L^{-1} HNO_3 to remove the traces of Ti, U and $K_2S_2O_8$, respectively. Neptunium is eluted with 15 mL 0.1 mol L^{-1} HCl / 0.04% oxalic acid.

Purification of the Pu fraction: The sample aliquot is loaded onto a DGA column and the column is washed with 5 mL 4 mol L^{-1} HCl. Plutonium is eluted with 15 mL 0.5 mol L^{-1} HCl.

Purification of the Th fraction: The concentration of the Th fraction (originally 2 mol L^{-1} HCl) is set to 4 mol L^{-1} HCl with concentrated HCl. The sample aliquot is loaded onto a DGA column and the column is washed with 5 mL 4 mol L^{-1} HCl. Thorium is eluted with 10 mL 0.1 mol L^{-1} HCl / 0.04% oxalic acid.

Purification of the U fraction: The acid concentration of the U fraction (originally 0.1 mol L^{-1} HCl / 0.1 mol L^{-1} HF) is set to 4 mol L^{-1} HCl with concentrated HCl and 100 mg H_3BO_3 is added to complex fluoride. The sample aliquot is loaded onto a DGA column and the column is washed with 6 mL 4 mol L^{-1} HCl. Uranium is eluted with 10 mL 0.1 mol L^{-1} HCl.

In all cases the purified fractions are measured directly by ICP-MS but if necessary (e.g. if the concentration of the measurand is low) the aliquot that is free of any non-volatile impurities can be evaporated to dryness and taken up in 1.5-2 mL 1% HNO_3.

3.2.7. Validation of the analytical procedure

3.2.7.1. Sample preparation for the validation

Test, swipe and environmental CRM samples were analyzed to test and validate the final analytical procedure.

In case of test samples (containing only tracers of actinides in 2 mol L^{-1} HNO_3) after the separation of the actinides using the method described in chapter 3.2.6. the fractions were divided: alpha sources were prepared directly from 100%, 90%, 15%, 90% and 80% of the Am, Pu, Th, Np and U fractions, respectively. The aliquots for ICP-MS were further purified according to the procedures described in chapter 3.2.6., they were converted to approximately 2 mL 1% HNO_3 form and diluted to avoid contamination of the ICP-MS. The dilution factors were 17, 5, 80 and 4 in case of the Pu, Th, Np and U sources, respectively.

The swipe samples (blank and reference) were ashed at 600 °C for ca. 20 h then dissolved with 65% HNO_3 and evaporated to dryness several times after addition of 65% HNO_3, 30%. H_2O_2, aqua regia and 65% HNO_3.The same tracers were used as in the case of the test samples. The preconcentration with CaF_2 was skipped. Only approximately 5% of the samples were analyzed further due to the relatively high U and Pu content (1 µg and 1 ng, respectively). The sample splitting following the actinide separation, was slightly different from that of the test samples: 100%, 90%, 20%, 90% and 50% of the Am, Pu, Th, Np and U fractions were analyzed by alpha spectrometry, respectively. After further purification the swipes were treated the same way as the test samples and the ICP-MS sources were also diluted. The dilution factors were 10, 4, 60 and 1000 in case of the Pu, Th, Np and U sources for ICP-MS, respectively.

In case of the environmental CRM samples approximately 0.5 g of the IAEA-135 CRM (Irish Sea sediment) was fused using a fluxer. Neptunium-239 was added as Np tracer besides ^{243}Am, ^{242}Pu, ^{229}Th and ^{233}U. It is a short lived (half-life: ~2.36 d) isotope which can be measured by gamma spectrometry (gamma lines at 106.1 keV (27.2%), 228.2 keV (10.8%) and 277.6 keV (14.4%)). Neptunium-239 tracer was milked from ^{243}Am retained on a DGA column [Groska 2012] right before starting the analysis. After the addition of tracers the pre-concentration was done according to our original method [1]. The Am, Pu and U fractions were divided immediately after the actinide separation: 100%, 90%, and 75% of the Am, Pu and U fractions were analyzed by alpha spectrometry, respectively. In case of the Th and the Np fractions, the sample splitting (90% and 50% of the Th and Np fractions for alpha

spectrometry, respectively) took place only after the purification by DGA since the Np recovery was determined by measuring the initial and the separated/purified Np fraction by gamma spectrometry; and due to the low concentration of the ^{229}Th tracer (~60 pg ^{229}Th / g sample besides ~9 µg ^{232}Th / g sample) the Th recovery could be only obtained by alpha spectrometry. After further purification the ICP-MS sources were also diluted. The dilution factors were 10, 9000, 100 and 10000 in case of the Pu, Th, Np and U sources for ICP-MS, respectively.

3.2.7.2. Results of the validation

3.2.7.2.1. Chemical recovery

The procedure was tested with test (Test-1, Test-2), swipe (Swipe-1, Swipe-2, Swipe-3 and environmental CRM samples (135-1, 135-2). The achieved chemical recoveries summarized in Table 8 were acceptable and repeatable. We assume that recoveries above 50% in a combined procedure (including decomposition, co-precipitation, main separation and purification, sample splitting, source preparation and measurements) for the simultaneous determination of several nuclides can be regarded as good.

Table 8 Obtained chemical recoveries

		Test-1 [%]	Test-2 [%]	Swipe-1 [%]	Swipe-2 [%]	Swipe-3 [%]	135-1 [%]	135-2 [%]
Am	**Alpha**	88%	69%	90%	90%	76%	86%	85%
	ICP-MS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pu	**Alpha**	89%	88%	94%	99%	96%	88%	86%
	ICP-MS	60%	70%	44%	54%	51%	44%	58%
Th	**Alpha**	97%	67%	86%	58%	68%	65%	65%
	ICP-MS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Np	**Alpha/Gamma**	52%	54%	65%	63%	58%	18%[a]	80%[1]
	ICP-MS	53%	36%	54%	58%	53%	n.d.	n.d.
U	**Alpha**	n.d.	n.d.	n.d.	n.d.	n.d.	69%	75%
	ICP-MS	58%	71%	56%	53%	50%	41%	51%

n.d.: not determined; [a] Recovery obtained by gamma spectrometry

The recoveries obtained by alpha spectrometry are higher than those obtained by ICP-MS because after the main separation on the TRU column the aliquots for ICP-MS were further purified on a DGA column; moreover the purified fractions were evaporated to dryness and fumed several times with 65% HNO_3 and 30% H_2O_2. These operations - especially evaporation of sample (containing trace elements) to dryness - could cause significant loss. The recoveries obtained by alpha measurements comprise the losses due to alpha source preparation that are typically less than 10%.

Americium was only measured by alpha spectrometry and recoveries were always high (≥69%). Plutonium recoveries measured by alpha spectrometry were always high (≥86%). Thorium recoveries were acceptably high (≥58%) according to alpha spectrometry. The recoveries for Np obtained by alpha or gamma spectrometry were acceptably high (≥52%) with one exception. In case of sample 135-1 the low Np recovery was attributed to the accidentally added low Ti^{4+} amount in the Th elution solution which could not oxidize all the Np to Np(VI). The Np recoveries obtained by ICP-MS were comparable with those obtained by alpha spectrometry. Significant losses during the multi-step source preparation for ICP-MS did not occur. The U recoveries were also acceptably high ((≥50%). Recoveries were not determined by alpha spectrometry in case of test and swipe samples. The recoveries in the environmental samples (135-1, 135-2) were acceptably high according to alpha spectrometric measurements.

Alpha peaks originating from other actinides were not observable in the alpha spectra of the given actinide fractions representing the high selectivity of the separations.

3.2.7.2.2. Detection limits

The detection limits (LD) were determined according to the International Standard of ISO/FDIS 11929 (2009) [ISO 2009]. The calculation is based on the decision threshold (DT) which can be calculated by multiplying the standard uncertainty of the final result when its value is zero ($\tilde{u}(0)$) with the quantity of the standardized normal distribution (k) for the probability of 1-α where α is the probability of the error of the first kind ($k_{1-\alpha} = 1.645$ at the confidence interval of 0.05): $DT = k_{1-\alpha} \cdot \tilde{u}(0)$ The detection limit was determined as the decision threshold multiplied by 2 (rough estimation).

The detection limit calculated by this method can be regarded as “extended” detection limit because it includes basically all the operations, measurement conditions (e.g. dilution of the final sources for ICP-MS or measurement time of the alpha spectrometry measurement) applied during the analysis. The detection limits of the investigated isotopes were calculated for the analysis of each sample since some parameters slightly differed from one sample to the other (e.g.: sample splitting, dilution of the ICP-MS source and alpha spectrometric measurement time). Table 9 summarizes the detection limits of each isotope determined in the IAEA-135 CRM. It has to be also mentioned that since the detection limits obtained by alpha spectrometry and ICP-MS were calculated using the same ISO method, the values can be directly compared.

Table 9 The detection limits of the analysis of sample 135-2

	LD alpha spec. [mBq/g]	LD ICP-MS [mBq/g]		LD alpha spec. [mBq/g]	LD ICP-MS [mBq/g]
^{241}Am	0.5	n.d.	**^{232}Th**	0.1	0.005
^{238}Pu	0.6	n.d.	**^{230}Th**	0.4	15
^{239}Pu	n.d.	0.4	**^{228}Th**	0.5	n.d.
^{240}Pu	n.d.	1.1	**^{234}U**	0.3[a]	0.38
^{241}Pu	n.d.	674	**^{235}U**	0.5	0.001
^{239,240}Pu	0.3	n.d.	**^{238}U**	0.5	0.004
^{237}Np	0.4	0.01			

n.d.: not determined; [a] if the ^{234}U / ^{233}U ratio is close enough to 1 (See chapter 3.2.7.)

Americium was only measured and ^{238}Pu could be only determined by alpha spectrometry. The ^{239}Pu, ^{240}Pu isotopes can be only determined separately by ICP-MS and alpha spectrometry is only capable of obtaining result for ^{239,240}Pu. The detection limit of ^{239,240}Pu is slightly better for alpha spectrometry since the final sources for ICP-MS had to be diluted 5 times to avoid introducing too high concentration of Pu into the mass spectrometer. Although ICP-MS has a significantly better detection limit for ^{232}Th, ^{228}Th is more sensitive to measure by alpha spectrometry compared to ICP-MS due to the low specific mass (or half-life). Higher detection limit for ^{230}Th was achieved by ICP-MS because the final sources for ICP-MS had to be diluted 5000 times due to the high ^{232}Th content. The detection limit for ^{237}Np is significantly better in case of ICP-MS. The detection limits for ^{234}U that can be obtained by alpha spectrometry and ICP-MS are basically the same but for the other U isotopes ICP-MS can result significantly lower detection limits. The alpha peak of the ^{233}U tracer overlaps with that of the ^{234}U therefore the ratio of the ^{234}U and ^{233}U has to be obtained from the ICP-MS measurement for the evaluation of the alpha spectra.

3.2.7.2.3. Validation of the analytical procedure

The isotope dilution technique was used to determine the actinide concentrations except for Th and Np obtained by ICP-MS. For the latter two results were calculated using external calibration by ^{229}Th and ^{237}Np, respectively assuming that the sensitivity of ^{229}Th equals that of ^{230}Th and ^{232}Th. In case of the U results originating from alpha spectrometry the ^{233}U tracer and the ^{234}U appear in the same alpha peak due to their similar alpha energies. The ^{234}U/^{233}U isotope ratio from the ICP-MS measurement was used to determine the alpha intensities of these isotopes to be able to obtain U alpha spectrometry results. It has to be mentioned if the ^{234}U/^{233}U isotope ratio is low, the uncertainty of the ^{234}U result will be unacceptably high.

The combined uncertainty of the results was calculated using Kragten's spreadsheet method [Kragten 1994].

As examples one-one set of results of the reference swipe and IAEA-135 CRM samples of the validation study are shown in the Table 10 and 11 together with their reference and information values.

Table 10 Results of the analysis of sample Swipe-3

	ICP-MS			Alpha spectrometry			Reference values at measurement date		
	Activity [Bq]	Unc (1σ) [Bq]	Rel Unc [%]	Activity [Bq]	Unc (1σ) [Bq]	Rel Unc [%]	Activity [Bq]	Unc (1σ) [Bq]	Rel Unc [%]
^{241}Am	n.d.	n.d.	n.d.	13.0	0.3	2.1%	10.2	0.7	7.1%
^{238}Pu	n.d.	n.d.	n.d.	3.0	0.2	5.6%	3.2	0.2	5.4%
^{239}Pu	23.0	0.8	3.4%	n.d.	n.d.	n.d.	24	1	5.0%
^{240}Pu	11.1	0.4	3.5%	n.d.	n.d.	n.d.	11.7	0.6	5.0%
^{241}Pu	115	16	13.8%	n.d.	n.d.	n.d.	115	6	5.0%
^{239,240}Pu	34.2	0.9	2.6%	31	1	4.6%	36	1	5.0%
^{234}U	0.0175	0.0006	3.3%		<LD		0.0143	0.0007	5.0%
^{235}U	0.00068	0.00002	2.3%		<LD		0.00065	0.00003	5.0%
^{238}U	0.0138	0.0003	2.3%		<LD		0.0135	0.0007	5.0%

n.d.: not determined; <LD: under the detection limit; Unc: uncertainty

Table 11 Results of the analysis of sample 135-2

	ICP-MS			Alpha spectrometry			Reference and information values at measurement date		
	Activity Conc. [Bq/g]	Unc (1σ) [Bq/g]	Rel Unc [%]	Activity Conc. [Bq/g]	Unc (1σ) [Bq/g]	Rel Unc [%]	Activity Conc. [Bq/g]	Unc (1σ) [Bq/g]	Rel Unc [%]
^{241}Am[6]	n.d.	n.d.	n.d.	0.389	0.009	2.4%	0.370[a,d]	0.063[d]	17.1%[d]
^{238}Pu	n.d.	n.d.	n.d.	0.036	0.002	6.6%	0.037	0.002	4.7%
^{239}Pu	0.130	0.007	5.6%	n.d.	n.d.	n.d.	-	-	-
^{240}Pu	0.095	0.005	5.7%	n.d.	n.d.	n.d.	-	-	-
^{241}Pu	1.325	0.249	18.8%	n.d.	n.d.	n.d.	-	-	-
^{239,240}Pu	0.225	0.009	4.0%	0.224	0.008	3.6%	0.213[b]	0.013	6.1%
^{228}Th[c]	n.d.	n.d.	n.d.	0.043	0.006	14.1%	0.035[d]	0.003[d]	9.0%[d]
^{230}Th[c]	0.11	0.03	30.6%	0.08	0.01	13.5%	0.069[d]	0.006[d]	9.0%[d]
^{232}Th[3]	0.041	0.006	13.7%	0.037	0.005	14.4%	0.037	0.001	4.1%
^{237}Np	0.0007	0.0001	12.3%		<LD		-	-	-
^{234}U[6]	0.026	0.001	5.5%	0.019	0.004	10.6%	0.028	0.006	19.6%
^{235}U[6]	0.0014	0.0001	4.6%	0.0012	0.0004	28.0%	0.0010	0.0003	31.0%
^{238}U[6]	0.030	0.001	4.7%	0.023	0.003	7.0%	0.030	0.005	15.8%

n.d.: not determined; Unc: uncertainty; [a] ^{241}Pu results were used from ICP-MS measurement for the calculation of ^{241}Am information value at measurement date; [b] Half life of ^{239}Pu was used for the calculation of ^{239,240}Pu reference value at measurement date; [c] All Th recoveries were obtained from alpha spectrometry; [d] Data are information values; <LD: under the detection limit; Unc: uncertainty

In case of swipe sample (Swipe 3) the results mostly agreed with the reference values within the uncertainty of the method, although bias between the reference values and the results of the ^{241}Am and ^{239,240}Pu obtained by alpha spectrometry and the results of ^{234}U obtained by ICP-MS could be observed: 27%, -14% and 22%, respectively while the uncertainties were 2.1%, 4.6% and 3.3%, respectively.

In case of IAEA-135 (135-2) sample the results agreed well with the reference and information values within the uncertainty of the method. The results of ^{239,240}Pu obtained by alpha spectrometry and ICP-MS agreed well and the uncertainties were comparable. The Th results showed not only better agreement with the information values but the obtained uncertainties were also lower in case of alpha spectrometry. In case of U results the ones obtained by ICP-MS showed better agreement and lower uncertainty.

The extraction chromatographic separation took significantly longer time for swipe than for the IAEA-135 CRM samples. For swipe samples no pre-concentration using CaF_2 co-precipitation was necessary and the excess of the reducing agents present in the load solution gave rise to bubbles forming on the TRU-columns causing slow eluent flow rates. To avoid loss of time and enhance the reproducibility, the pre-concentration (to separate the reduction and oxidation steps) is advised for swipe samples, as well.

3.2.8. Conclusions

The improved radioanalytical procedure is capable of the simultaneous separation of Th, U, Np, Pu and Am(Cm) on a single TRU column while in the literature more extraction chromatographic and/or ion exchange columns are used to achieve this objective. The separation is based on the selective on-column oxidation state adjustment of actinides instead of the use of complexing agents which are not 'actinide-selective'. Moreover with the combination of alpha spectrometry and ICP-MS more information can be obtained because some isotopes can be determined only by one technique (e.g. ^{228}Th, ^{238}Pu... only by alpha spectrometry; ^{235}U, ^{241}Pu... only by ICP-MS) therefore the number of the examined isotopes is broadened. More accurate results can also be obtained because some isotopes can be determined by both techniques (e.g. ^{230}Th, ^{234}U, ^{238}U...) and the comparison of the results can improve the reliability. A really wide range of isotopes can be determined: ^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, (^{236}U), ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am, ^{242}Cm, ^{243}Cm and ^{244}Cm.

The model experiments revealed some interesting properties of the TRU extraction chromatographic resin. Although in some cases the oxidation state of actinides can be

adjusted on the TRU column using the proper redox reagent: e.g. Ti(IV) can adjust Np(IV) to Np(VI) while Ti(III) Np(VI) to Np(IV) and Pu(IV) to Pu(III), the odd oxidation states of Np cannot be adjusted on the TRU column even if pentavalent state is the most stable oxidation state of Np in aqueous solutions. Titanium was also proved to improve the elution of tetravalent actinides. According to the results of the model experiment it can be assumed that Ti, as analogue helps remove Th by co-elution.

3.3. Method development for the determination of low level ^{238}Pu in safeguards swipe samples by alpha spectrometry using ICP MS results of ^{239}Pu and ^{240}Pu

3.3.1. The objective of the study

The objective of this study was to modify the standard procedure of the IAEA Clean Laboratory (Fig. 1) without implementing any serious modification in order to analyze ^{238}Pu in a limited amount of samples with the combination of alpha spectrometry and ICP-MS.

According to my original idea the ^{238}Pu and ^{239,240}Pu ratio can be determined accurately by counting the alpha sources prepared from a given part of the sample aliquots for isotope ratio analysis ('Pu ISO') which do not contain Pu tracer (see chapter 2.1.3.). The activity and the amount of ^{238}Pu can be calculated from the accurately determined amount of ^{239}Pu and ^{240}Pu obtained by the ICP-MS measurements of sample aliquot for quantitative analysis ('Pu IDA') which contains Pu tracer and the ^{238}Pu and ^{239,240}Pu ratio determined by alpha spectrometry. See Fig. 1. The calculation methods of the results including the uncertainties were determined in detail and the method was tested by the analysis of test samples containing approximately 130 and 250 fg ^{238}Pu and real inspection samples collected by safeguards inspectors. The achievable accuracy and precision were examined, as well; moreover the main components of the uncertainty of the final results were determined in case of each sample type.

3.3.2. Equipment

The mass spectrometric analysis was carried out using a Thermo Electron Element 2 ICP-MS with magnetic sector field. All measurements were carried out in low resolution mode using a PFA micro-flow nebulizer in self-aspirating mode. The conditions of the measurements were: plasma power: 1250 W, sample gas rate: 0.8-0.9 L min^{-1}, auxiliary gas rate: 1.2-1.3 L min^{-1} and cooling gas rate: 16 L min^{-1}.

The alpha spectrometry system (Canberra Alpha Analyst, Model 7200-12; S/N: 02084558) with alpha passivated implanted planar silicon (PIPS) detectors (A 450-18 AM) having the active area of 450 mm^2, Canberra Alpha Analyst analyzer and GENIE 2000 alpha spectroscopy software were used for the alpha spectrometry measurements. The efficiency of the detectors at the position used in this study was typically 25 %.

3.3.3. Reagents and materials

Test samples were prepared from the standard reference material NBL CRM 137 [CRM-137] that is a mixture of Pu isotopes in HNO_3 solution. The certified abundance of each Pu isotope in NBL CRM 137 (in weight %) is ^{238}Pu: 0.229 ± 0.005, ^{239}Pu: 78.707 ± 0.034, ^{240}Pu: 19.041 ± 0.024, ^{241}Pu: 0.779 ± 0.002 and ^{242}Pu: 1.244 ± 0.004 (corrected to April, 2009). Isotopic reference materials, IRMM-044 (^{242}Pu tracer, 1998) [IRMM-044] and CBNM IRM-042a (^{244}Pu tracer, 1989) [IRM-042a] were used as tracer and internal standard for the ICP-MS measurements, respectively. NBL CRM-128 (New Brunswick Laboratory, Argonne, Illinois, USA: ^{239}Pu/^{242}Pu = 0.9987 at the measurement date (February 2009) was used for mass bias correction. High purity HNO_3, HCl, and HBr (Seastar Chemicals Inc., Canada); 18.2 MΩ de-ionized water (Milli-Q Element), analytical grade HF and H_2O_2 (Seastar Chemicals Inc., Canada) were used for the chemical treatment. The anion-exchange resin of AG MP-M1® (50-100 mesh, BioRad®) was used for chemical separation. The resin was filled into BioRad® columns (inner diameter approximately 0.8 mm).

3.3.4. Samples

Two batches of test samples were prepared from NBL CRM 137 containing approximately 130 fg (approximately 80 mBq) and approximately 250 fg (approximately 160 mBq) of ^{238}Pu. Water samples from safeguards inspections as real samples were also analyzed.

3.3.5. Sample preparation

In the *test samples*, ^{241}Am was produced by beta decay of ^{241}Pu. Because of the similar alpha particle energy of the ^{241}Am (5486 keV) and the ^{238}Pu (5499 keV), their alpha peaks cannot be decomposed in the alpha spectrum. Therefore for the further examination the ^{241}Am had to be removed by the standard procedure of the IAEA Clean Laboratory (see chapter 2.3.1.).

After adding known amount of ^{242}Pu tracer, test samples were heated to dryness and taken up in 2 mL 10 mol L^{-1} HCl / H_2O_2 as load solutions. BioRad® columns were filled with 2 mL AG MP-1® ion exchange resin and first washed with 10 mL 18.2 MΩ MilliQ de-ionized water, 10 mL 8 mol L^{-1} HNO_3 and 10 mL 0.5 mol L^{-1} HCl and finally conditioned with 10 mL 10 mol L^{-1} HCl. After loading the samples, the columns were rinsed with 30 mL 10 mol L^{-1} HCl / H_2O_2. The Pu was eluted with 20 mL concentrated HBr. The Pu fractions were heated

to dryness and fumed first with concentrated HNO_3 and H_2O_2, finally with only concentrated HNO_3. The samples were taken up in 2 mL 1 mol L^{-1} HNO_3 to divide them into two parts: approximately 1% was used for ICP-MS measurement. The aliquot was diluted to 2 mL with 18.2 MΩ MilliQ de-ionized water. Alpha sources were prepared by micro co-precipitation with NdF_3 [Hindman 1986] from approximately 99% of the test samples for alpha spectrometry. The alpha aliquots were heated to dryness then taken up in 1.3 mL concentrated HNO_3 and diluted to 20 mL with 18.2 MΩ MilliQ de-ionized water. After adding 50 µg Nd^{3+}, 1 mL 25% $NaNO_3$ and 5 mL concentrated HF the samples were filtered onto a cellulose nitrate membrane (0.2 µm pore size, 25 mm diameter, Pall Corporation).

For *inspection samples*, Pu was separated from U, Am and other nuclides following the standard procedure of the IAEA Clean Laboratory (see chapter 2.3.1.). Approximately 20% of the sample aliquots were used for ICP-MS measurement and approximately 5% was used for alpha spectrometry measurement. Alpha sources were prepared by the procedure applied for test samples. (There was no need for purification of the Pu fractions because Am had been removed in standard procedure performed just before alpha analysis.)

3.3.6. Calculations

3.3.6.1. Corrections of the ICP-MS results

First of all, the decay corrections were made to April 2009 for each reference material (NBL CRM-137, IRMM-044 and CBNM IRM-042a) used in this study.

Secondly, 'intensity correction' factors were calculated for ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu since the reference materials contained each Pu isotope. E.g. the measured intensity of ^{242}Pu originated not only from IRMM-044 but from NBL CRM-137 and CBNM IRM-042a, as well in case of test samples. Therefore for further calculations, the intensity originating only from the known amount of added ^{242}Pu tracer had to be known. These corrections had to be done after the background subtraction for all the measured intensities obtained by ICP-MS and alpha spectrometry in case of each Pu isotope. For the raw results obtained by ICP-MS, the additional intensities of the ^{242}Pu originating from the IRMM-044 tracer were not taken into account because this correction was performed in the latter isotope dilution calculations (Eq. 6, 7 and 12) of the amount of the Pu isotopes.

Internal standard corrections were also done after the 'intensity correction'. Known amount of ^{244}Pu, as internal standard was added to each sample aliquot for ICP-MS and the

intensities of the Pu isotopes were corrected with the intensities of the ^{244}Pu calculated to 1 pg g^{-1}.

Finally, the mass discrimination was determined by measuring 1 pg g^{-1} of NBL CRM-128 (New Brunswick Laboratory, Argonne, Illinois, USA: ^{239}Pu/^{242}Pu = 0.9987 at the measurement date) ten times. The bias correction factor (BCF) calculated with the formula of Bayne [Bayne 1996] (Eq. 4) was 0.0003:

$$BCF = \frac{\frac{N_{242}}{N_{239}} \cdot R_{ref} - 1}{\Delta M}, \quad (4)$$

where N_{242} and N_{239} are the count rates of ^{242}Pu and ^{239}Pu, respectively, R_{ref} is the reference value of ^{239}Pu / ^{242}Pu of the measured certified reference material and ΔM is the mass difference between ^{239}Pu and ^{242}Pu (239-242 = -3). The BCF_i for each Pu isotope ratio was calculated: $BCF_i = BCF \cdot \Delta M$, where BCF_i is $BCF_{239/242}$, $BCF_{240/242}$ and $BCF_{241/242}$.

The dead time correction for ICP-MS was automatically performed by the software of the instrument according to the next equation:

$$N_{corr} = \frac{N_{meas}}{1 - N_{meas} \cdot \tau}, \quad (5)$$

where N_{corr} and N_{meas} are the corrected and measured count rates and τ is the detector dead time (τ = 10 ns).

3.3.6.2. Determination of the activity and the amount of ^{238}Pu

The amount of ^{239}Pu (m_{Pu-239}, [g]) and ^{240}Pu (m_{Pu-240}, [g]) were calculated from the results of ICP-MS measurements according to Eq. 6 and 7.

$$m_{Pu-239} = \frac{m_{Pu-242} \frac{M_{Pu-239}}{M_{Pu-242}} \left[\left(\frac{Pu-239}{Pu-242} \right)_{sample} \times (1 + BCF_{239/242}) - \left(\frac{Pu-239}{Pu-242} \right)_{tracer} \times (1 + BCF_{239/242}) \right]}{R_{sample}}, \quad (6)$$

$$m_{Pu-240} = \frac{m_{Pu-242} \frac{M_{Pu-240}}{M_{Pu-242}} \left[\left(\frac{Pu-240}{Pu-242} \right)_{sample} \times (1 + BCF_{240/242}) - \left(\frac{Pu-240}{Pu-242} \right)_{tracer} \times (1 + BCF_{240/242}) \right]}{R_{sample}}, \quad (7)$$

where m_{Pu-242} is the amount of ^{242}Pu tracer [g] added to the sample aliquot as tracer for quantitative analysis performed by ICP-MS (Pu IDA); $\frac{M_{Pu-239}}{M_{Pu-242}}$ and $\frac{M_{Pu-240}}{M_{Pu-242}}$ are the ratios of the molar masses [-] of ^{239}Pu and ^{242}Pu and ^{240}Pu and ^{242}Pu, respectively;

$\left(\frac{Pu-239}{Pu-242}\right)_{sample} \times (1+BCF_{239/242})$ and $\left(\frac{Pu-240}{Pu-242}\right)_{sample} \times (1+BCF_{240/242})$ are the background, internal standard and mass bias corrected intensity ratios of ^{239}Pu and ^{242}Pu and ^{240}Pu and ^{242}Pu in the sample (background measurements were performed before each sample measurement), respectively; $\left(\frac{Pu-239}{Pu-242}\right)_{tracer} \times (1+BCF_{239/242})$ and $\left(\frac{Pu-240}{Pu-242}\right)_{spike} \times (1+BCF_{240/242})$ are the mass bias corrected intensity ratios of ^{239}Pu and ^{242}Pu and ^{240}Pu and ^{242}Pu in the tracer solution, respectively; R_{sample} is the aliquot of sample fraction used for Pu IDA sample aliquot.

The amount of ^{239}Pu (m_{Pu-239}, [g]) and ^{240}Pu (m_{Pu-240}, [g]) were converted to activity (A^{MS}_{Pu-239} [Bq], A^{MS}_{Pu-240} [Bq]) by the equation of $A = \lambda N = \frac{\ln(2)}{T_{1/2}} \frac{m}{M} N_A$, where $T_{1/2}$ is the half life and N_A is the Avogadro number. The activities of ^{239}Pu and ^{240}Pu were added for the further calculations ($A^{MS}_{Pu-239,240} = A^{MS}_{Pu-239} + A^{MS}_{Pu-240}$).

Alpha sources of Pu were counted and the intensity ratios of ^{238}Pu and ^{239,240}Pu ($\frac{I^{\alpha}_{Pu-238}}{I^{\alpha}_{Pu-239,240}}$) were calculated. The activity of the ^{238}Pu was calculated using the following equation (Eq. 8):

$$\frac{A_{Pu-238}}{A^{MS}_{Pu-239,240}} = \frac{I^{\alpha}_{Pu-238}}{I^{\alpha}_{Pu-239,240}}, \quad (8)$$

where I^{α}_{Pu-238} and $I^{\alpha}_{Pu-239,240}$ are the intensities of ^{238}Pu and ^{239,240}Pu [cps], respectively; $A^{MS}_{Pu-239,240}$ is the activity of ^{239,240}Pu calculated from the results obtained by ICP-MS and A_{Pu-238} is the activity of the ^{238}Pu in the sample which was converted to mass (m_{Pu-238} [g])

3.3.6.3. Additional calculations

The amount of ^{241}Pu (m_{Pu-241}, [g]) was also calculated from the results of ICP-MS measurements according to Eq. 9:

$$m_{Pu-241} = \frac{m_{Pu-242} \frac{M_{Pu-241}}{M_{Pu-242}} \left[\left(\frac{Pu-241}{Pu-242}\right)_{sample} \times (1+BCF_{241/242}) - \left(\frac{Pu-241}{Pu-242}\right)_{tracer} \times (1+BCF_{241/242}) \right]}{R_{sample}}, \quad (9)$$

where $\frac{M_{Pu-241}}{M_{Pu-242}}$ is the ratio of the molar masses [-] of ^{241}Pu and ^{242}Pu; $\left(\frac{Pu-241}{Pu-242}\right)_{sample} \times (1+BCF_{241/242})$ is the background, internal standard and mass bias corrected intensity ratio of ^{241}Pu and ^{242}Pu in the sample; $\left(\frac{Pu-241}{Pu-242}\right)_{tracer} \times (1+BCF_{241/242})$ is the mass bias corrected intensity ratio of ^{241}Pu and ^{242}Pu in the tracer solution. The amount of ^{241}Pu (m_{Pu-241}, [g]) was also converted to activity (A^{MS}_{Pu-241} [Bq]).

3.3.6.4. Uncertainty calculations

The uncertainties were calculated according to the law of the uncertainty propagation. This law was applied through the whole calculation method: from the decay corrections of the reference materials to the final results. Only the uncertainties of molar masses, correction factors (mass bias, dead-time, 'intensity'; see chapter 3.3.6.1.) were not taken into account. Only the uncertainties of the main elements of the calculations will be discussed in detail.

The uncertainty of m_{Pu-239}, m_{Pu-240} and m_{Pu-241} were calculated according to the following equations (Eq. 10-12):

$$\sigma^2_{m_{Pu-239}} = \left(\frac{\frac{M_{Pu-239}}{M_{Pu-242}}\left(\frac{Pu-239}{Pu-242}\right)_{sample} - \frac{M_{Pu-239}}{M_{Pu-242}}\left(\frac{Pu-239}{Pu-242}\right)_{tracer}}{R_{sample}} \right)^2 \sigma^2_{m_{Pu-242}} + \left(-\frac{m_{Pu-242}\frac{M_{Pu-239}}{M_{Pu-242}}}{R_{sample}} \right)^2 \sigma^2_{\left(\frac{Pu-239}{Pu-242}\right)_{tracer}} + \left(\frac{m_{Pu-242}\frac{M_{Pu-239}}{M_{Pu-242}}}{R_{sample}} \right)^2 \sigma^2_{\left(\frac{Pu-239}{Pu-242}\right)_{sample}} \quad (10)$$

$$\sigma^2_{m_{Pu-240}} = \left(\frac{\frac{M_{Pu-240}}{M_{Pu-242}}\left(\frac{Pu-240}{Pu-242}\right)_{sample} - \frac{M_{Pu-240}}{M_{Pu-242}}\left(\frac{Pu-240}{Pu-242}\right)_{tracer}}{R_{sample}} \right)^2 \sigma^2_{m_{Pu-242}} + \left(-\frac{m_{Pu-242}\frac{M_{Pu-240}}{M_{Pu-242}}}{R_{sample}} \right)^2 \sigma^2_{\left(\frac{Pu-240}{Pu-242}\right)_{spike}} + \left(\frac{m_{Pu-242}\frac{M_{Pu-240}}{M_{Pu-242}}}{R_{sample}} \right)^2 \sigma^2_{\left(\frac{Pu-240}{Pu-242}\right)_{sample}} \quad (11)$$

$$\sigma^2_{m_{Pu-241}} = \left(\frac{\frac{M_{Pu-241}}{M_{Pu-242}}\left(\frac{Pu-241}{Pu-242}\right)_{sample} - \frac{M_{Pu-241}}{M_{Pu-242}}\left(\frac{Pu-241}{Pu-242}\right)_{tracer}}{R_{sample}} \right)^2 \sigma^2_{m_{Pu-242}} +$$
$$+ \left(-\frac{m_{Pu-242}\frac{M_{Pu-241}}{M_{Pu-242}}}{R_{sample}} \right)^2 \sigma^2_{\left(\frac{Pu-241}{Pu-242}\right)_{tracer}} + \left(\frac{m_{Pu-242}\frac{M_{Pu-241}}{M_{Pu-242}}}{R_{sample}} \right)^2 \sigma^2_{\left(\frac{Pu-241}{Pu-242}\right)_{sample}} \quad (12)$$

where $\left(\frac{Pu-239}{Pu-242}\right)_{sample}$, $\left(\frac{Pu-240}{Pu-242}\right)_{sample}$ and $\left(\frac{Pu-241}{Pu-242}\right)_{sample}$ are the background, internal standard and mass bias corrected intensity ratios of ^{239}Pu and ^{242}Pu; ^{240}Pu and ^{242}Pu and ^{241}Pu and ^{242}Pu, respectively; σ_i^2 is the square of the absolute uncertainty of the given value. The $\sigma^2_{\left(\frac{Pu-239}{Pu-242}\right)_{tracer}}$, $\sigma^2_{\left(\frac{Pu-240}{Pu-242}\right)_{tracer}}$ and $\sigma^2_{\left(\frac{Pu-241}{Pu-242}\right)_{tracer}}$ were given in the certificate of the tracer solution.

The error propagation of the conversion from amount to activity and the addition of A^{MS}_{Pu-239} and A^{MS}_{Pu-240} was calculated using Eq. 13:

$$\boldsymbol{\sigma}^2_{A^{MS}_{Pu-239,240}} = \left(\frac{N_A}{M_{Pu-239}} \frac{\ln(2)}{T^{Pu-239}_{1/2}} \right)^2 \boldsymbol{\sigma}^2_{m_{Pu-239}} + \left(-\frac{m_{Pu-239} N_A \ln(2)}{M_{Pu-239}\left(T^{Pu-239}_{1/2}\right)^2} \right)^2 \boldsymbol{\sigma}^2_{T^{Pu-239}_{1/2}}$$
$$+ \left(\frac{N_A}{M_{Pu-240}} \frac{\ln(2)}{T^{Pu-240}_{1/2}} \right)^2 \boldsymbol{\sigma}^2_{m_{Pu-240}} + \left(-\frac{m_{Pu-240} N_A \ln(2)}{M_{Pu-240}\left(T^{Pu-240}_{1/2}\right)^2} \right)^2 \boldsymbol{\sigma}^2_{T^{Pu-240}_{1/2}} \quad (13)$$
$$+ \left(\frac{m_{Pu-239}}{M_{Pu-239}} \frac{\ln(2)}{T^{Pu-239}_{1/2}} + \frac{m_{Pu-240}}{M_{Pu-240}} \frac{\ln(2)}{T^{Pu-240}_{1/2}} \right)^2 \sigma^2_{N_A}$$

The uncertainty of the activity ^{241}Pu (A^{MS}_{Pu-241}) was calculated using the following equation:

$$\sigma^2_{A^{MS}_{Pu-241}} = \left(\frac{N_A}{M_{Pu-241}} \frac{\ln(2)}{T^{Pu-241}_{1/2}} \right)^2 \sigma^2_{m_{Pu-241}} + \left(-\frac{m_{Pu-241} N_A \ln(2)}{M_{Pu-241}\left(T^{Pu-241}_{1/2}\right)^2} \right)^2 \sigma^2_{T^{Pu-241}_{1/2}} + \left(\frac{m_{Pu-241}}{M_{Pu-241}} \frac{\ln(2)}{T^{Pu-241}_{1/2}} \right)^2 \sigma^2_{N_A} \quad (14)$$

The relative uncertainties ($\sigma^{\alpha}_{I_{Pu-238}}$, $\sigma^{\alpha}_{I_{Pu-239,240}}$) of the intensities I^{α}_{Pu-238} and $I^{\alpha}_{Pu-239,240}$ were equal to the relative uncertainties of number of counts in the given peak, therefore the relative uncertainties were taken as the square roots of the number of counts.

The uncertainty of the ^{238}Pu activity ($\sigma_{A_{Pu-238}}$) was calculated using Eq. 15.

$$\sigma^2_{A_{Pu-238}} = \left(\frac{A^{MS}_{Pu-239,240}}{I^{\alpha}_{Pu-239,240}}\right)^2 \left(\sigma^{\alpha}_{I_{Pu-238}}\right)^2 + \left(\frac{I^{\alpha}_{Pu-238}}{I^{\alpha}_{Pu-239,240}}\right)^2 \left(\sigma^{MS}_{A_{Pu-239,240}}\right)^2 + \left(-\frac{I^{\alpha}_{Pu-238} \cdot A^{MS}_{Pu-239,240}}{\left(I^{\alpha}_{Pu-239,240}\right)^2}\right)^2 \left(\sigma^{\alpha}_{I_{Pu-239,240}}\right)^2, \quad (15)$$

where $\sigma^{\alpha}_{I_{Pu-238}}$, $\sigma^{\alpha}_{I_{Pu-239,240}}$ are the uncertainties of the measured intensities of ^{238}Pu and ^{239,240}Pu by alpha spectrometry, respectively and $\sigma^{MS}_{A_{Pu-239,240}}$ is the uncertainty of the calculated sum activity of ^{239}Pu and ^{240}Pu from the ICP-MS measurement.

The uncertainty of the ^{238}Pu amount ($\sigma_{m_{Pu-238}}$) was calculated using Eq. 16.

$$\sigma^2_{m_{Pu-238}} = \left(\frac{M_{Pu-238}}{N_A}\frac{T^{Pu-238}_{1/2}}{\ln(2)}\right)^2 \sigma^2_{A_{Pu-238}} + \left(\frac{M_{Pu-238}}{N_A}\frac{A_{Pu-238}}{\ln(2)}\right)^2 \sigma^2_{T^{Pu-238}_{1/2}} + \left(-\frac{M_{Pu-238}T^{Pu-238}_{1/2}}{(N_A)^2\ln(2)}\right)^2 \sigma^2_{N_A} \quad (16)$$

3.3.7. Results and discussion

3.3.7.1. Test samples

Two groups of triplicate test samples were prepared containing different amounts of Pu isotopes. The reference values are shown in Table 12.

The recoveries of the chemical procedure varied between 83 and 93%.

The results of the measurements of the test samples are shown in Table 13. The measured values are in good agreement with the reference values within the uncertainties except in case of ^{241}Pu. The significant positive bias could be caused by polyatomic interferences (e.g. $^{206}Pb^{35}Cl$, $^{204}Hg^{37}Cl$, $^{200}Hg^{40}Ar$ originating mainly from chemicals). The presence of ^{241}Am is not likely since the results of ^{238}Pu were in good agreement with the reference values.

The bias between the measurements and the reference values ranges 0.1–4% and 0.01–4% for group A and group B, respectively. The relative uncertainties of the final results ranged from 3 to 20% except for sample A-3 and B-3 (9–21%, 25–38%, respectively). These high uncertainties were caused by the lower sensitivity of the ICP-MS measurement than that of the other measurements.

The relative uncertainties of ^{239,240}Pu and ^{238}Pu intensities measured by alpha spectrometry with a counting time of 48 h were less than 2%.

The uncertainties of the final results originated mainly from the intensities measured by ICP-MS measurements.

3.3.7.2. Inspection samples

Three water samples from safeguards inspections were analyzed as real samples using the standard radioanalytical procedure (Fig. 1) of the IAEA Clean Laboratory for the determination of U and Pu in environmental samples. No information was available about the origin of samples. The results are shown in Table 14 and 15.

The relative uncertainties of the final results ranged from 2.8 to 6.9%.

Since only approximately 5% of the whole samples was used for the determination of the isotope ratio of ^{238}Pu and ^{239,240}Pu by alpha spectrometry, long measurement times (1 000 000 s) were applied to achieve appropriate counting statistics (~5%) for the ^{238}Pu intensities. The sample aliquot for alpha spectrometry contained only 2-3 mBq ^{238}Pu. Hence the uncertainty of the final ^{238}Pu results originated mainly from the alpha spectrometry measurements.

The atom and activity ratios obtained from the inspection samples are shown in Table 16 and 17. The results indicate that the samples contain relatively low burn-up Pu (See chapter 2.1.4.).

Table 12 The reference values of the test samples

	m_{Pu-238}				m_{Pu-239}				m_{Pu-240}				m_{Pu-241}			
	[pg±unc_{PE}]			unc_{rel} [%]	[pg±unc_{PE}]			unc_{rel} [%]	[pg±uc_{PE}]			unc_{rel} [%]	[pg±uc_{PE}]			unc_{rel} [%]
A-1	0.132	±	0.025	18.6	45.6	±	8.4	18.5	11.0	±	2.0	18.5	0.45	±	0.08	18.5
A-2	0.132	±	0.025	18.6	45.3	±	8.4	18.5	11.0	±	2.0	18.5	0.45	±	0.08	18.5
A-3	0.133	±	0.025	18.6	45.6	±	8.4	18.5	11.0	±	2.0	18.5	0.45	±	0.08	18.5
B-1	0.259	±	0.048	18.6	89.1	±	16.5	18.5	21.6	±	4.0	18.5	0.88	±	0.16	18.5
B-2	0.254	±	0.047	18.6	87.5	±	16.1	18.5	21.2	±	3.9	18.5	0.87	±	0.16	18.5
B-3	0.259	±	0.048	18.6	89.0	±	16.4	18.5	21.5	±	4.0	18.5	0.88	±	0.16	18.5

* unc: uncertainty represents 1 σ

Table 13 The results of the test samples

	m_{Pu-238}				m_{Pu-239}				m_{Pu-240}				m_{Pu-241}			
	[pg±uc_{PE}]			unc_{rel} [%]	[pg±unc_{PE}]			unc_{rel} [%]	[pg±uc_{PE}]			unc_{rel} [%]	[pg±uc_{PE}]			unc_{rel} [%]
A-1	0.131	±	0.007	5	45.1	±	2.8	6	11.1	±	0.8	7	1.3	±	0.3	20
A-2	0.132	±	0.007	5	45.0	±	2.9	6	11.4	±	0.8	7	2.1	±	0.4	17
A-3	0.132	±	0.012	9	45.0	±	5.7	13	11.3	±	1.4	12	1.2	±	0.2	21
B-1	0.254	±	0.011	4	87.4	±	4.3	5	21.5	±	1.2	6	1.5	±	0.2	14
B-2	0.250	±	0.008	3	86.8	±	2.7	3	21.7	±	0.8	4	1.2	±	0.2	16
B-3	0.256	±	0.063	25	87.6	±	30.4	35	21.8	±	7.6	35	1.0	±	0.4	38

* unc: uncertainty represents 1 σ

Table 14 The results of the safeguards inspection samples – the concentration of the measured Pu isotopes [fg/g]

	m_{Pu-238}				m_{Pu-239}				m_{Pu-240}				m_{Pu-241}			
	[fg/g ± $unc_{fg/g}$*]			unc_{rel} [%]	[fg/g ± $unc_{fg/g}$]			unc_{rel} [%]	[fg/g ± $unc_{fg/g}$]			unc_{rel} [%]	[fg/g ± $unc_{fg/g}$]			unc_{rel} [%]
A	5.10	±	0.28	5.6	31892	±	895	2.8	2897	±	82	2.8	40.2	±	1.3	3.3
B	5.62	±	0.28	5.0	31855	±	1001	3.1	2904	±	92	3.2	40.4	±	2.8	6.9
C	4.08	±	0.22	5.3	29506	±	840	3.0	2683	±	81	3.0	37.5	±	1.8	4.7

* unc: uncertainty represents 1 σ

Table 15 The results of the safeguards inspection samples – the concentration of the measured Pu isotopes [mBq/g]

	A_{Pu-238}				A_{Pu-239}				A_{Pu-240}				A_{Pu-241}			
	[mBq/g ± $unc_{mBq/g}$*]			unc_{rel} [%]	[mBq/g ± $unc_{mBq/g}$]			unc_{rel} [%]	[mBq/g ± $unc_{mBq/g}$]			unc_{rel} [%]	[mBq/g ± $unc_{mBq/g}$]			unc_{rel} [%]
A	3.23	±	0.18	5.6	73.2	±	2.1	2.8	24.3	±	0.7	2.8	154	±	5	3.3
B	3.56	±	0.18	5.0	73.1	±	2.3	3.1	24.4	±	0.8	3.2	155	±	11	6.9
C	2.58	±	0.14	5.3	67.7	±	1.9	2.8	22.5	±	0.7	3.0	144	±	7	4.7

* unc: uncertainty represents 1 σ

Table 16 The Pu atom ratios in the safeguards inspection samples (calculated from the concentration results)

	^{238}Pu / ^{239}Pu				^{240}Pu / ^{239}Pu				^{241}Pu / ^{239}Pu			
	[-± unc.]			unc_{rel} [%]	[-± unc.]			unc_{rel} [%]	[-± unc.]			unc_{rel} [%]
A	0.00016	±	0.00001	6.3	0.0908	±	0.0030	3.3	0.0013	±	0.0001	4.3
B	0.00018	±	0.00001	5.9	0.0912	±	0.0033	3.7	0.0013	±	0.0001	7.6
C	0.00014	±	0.00001	6.1	0.0909	±	0.0031	3.5	0.0013	±	0.0001	5.6

Table 17 The Pu activity ratios in the safeguards inspection samples

	^{238}Pu / ^{239}Pu				^{240}Pu / ^{239}Pu				^{241}Pu / ^{239}Pu				^{238}Pu / $^{239+240}Pu$			
	[-± unc.]			unc_{rel} [%]	[-± unc.]			unc_{rel} [%]	[-± unc.]			unc_{rel} [%]	[-± unc.]			unc_{rel} [%]
A	0.0441	±	0.0028	6.3	0.3320	±	0.0131	4.0	2.1038	±	0.0927	4.4	0.0331	±	0.0020	6.0
B	0.0487	±	0.0029	5.9	0.3338	±	0.0149	4.5	2.1204	±	0.1604	7.6	0.0365	±	0.0020	5.6
C	0.0381	±	0.0023	6.0	0.3323	±	0.0136	4.1	2.1270	±	0.1164	5.5	0.0286	±	0.0016	5.8

3.3.8. Conclusions

The accuracy and the precision of ^{238}Pu determination at the fg level by alpha spectrometry using the results of ^{239}Pu and ^{240}Pu measurements obtained by ICP-MS were studied with the standard reference material. The results show that approximately 130 fg of ^{238}Pu can be analyzed accurately with a maximum 4% bias and an uncertainty of 5%.

The analysis of safeguards inspection samples demonstrated that less than 10 fg of ^{238}Pu in environmental water samples can be determined within 6% of total uncertainty applying the analytical method described in this study.

The combination of alpha spectrometry and ICP-MS applied in this study enables the ^{238}Pu determination which can enhance the reliability of the final conclusions of the analytical results of the safeguards inspection samples – regarding the nuclear activity in the nuclear facility (the sample origin).

3.4. Method development for the determination of U isotopic composition of single particles originating from safeguards swipe samples

3.4.1. The objectives of the study

Although swipe sampling has been routinely used as an effective inspection tool by the IAEA since 1996 to verify the absence of undeclared nuclear materials and activities, particle analysis has got only recently into the focus. Bulk analysis provides information only about the average composition of the samples however the artificial fissile material in the environment mostly occurs in the form of solid, radioactive particles.

My objective was to develop a complex method for the determination of the U isotopic composition of single particles originating from safeguards swipe samples. The method was planned to be built up several, individual procedures which can be combined easily with each other and with analysis by SEM, alpha spectrometry and/or gamma spectrometry: procedure for (1) particle removal from swipe samples, (2) the identification of particles containing alpha emitting and fissile material using solid state nuclear track detectors, (3) the localization and relocalization of identified particles, (4) the micromanipulation of particles and (5) the analysis of single particles by LA-ICP-MS. Each procedure was developed and tested separately and the whole method was also tested with different combinations using U test particles and particles originating from confiscated nuclear fuel pellets.

3.4.2. Equipment

Solid state nuclear track detectors produced by the Radosys Ltd were used. The surface of the detectors was 100 mm^2 and the thickness was 1 mm. Digit codes and dot marks can be found on the active surface [Hülber 2006]. The material of the track detector is so-called PADC/CR-39: radon and thoron sensitive polyallyl diglycol carbonate with a typical background of 0.1-0.5 track/mm^2. [CR-39]

The optical microscopes used were the optical microscope of the laser ablation system (New Wave Research, Freemont, USA) and a Zeiss® Axio Imager.M1m optical research microscope (Zeiss, Germany) equipped with an AxioCam MRc 5 video camera. The Zeiss microscope was equipped also with a micromanipulation system (Mitutoyo, Japan) placed on a vibration resistant stage (???). The scanning electron microscope used was a JEOL JSM-5600LV type scanning electron microscope. The magnifying range is 18× - 300,000×, the

maximum accelerating voltage is 30 kV. The SEM is equipped with an EDS2000 type energy dispersive micro-analyzer (IXRF Systems).

The mass spectrometric analysis was carried out using an Element 2 ICP-MS (Thermo Electron Corp., Germany) with magnetic sector field and single electron multiplier. The laser ablation was carried out using an UP-213 laser ablation system (New Wave Research, Freemont, USA) equipped with a Nd:YAG laser at a wavelength of 213 nm (pulse duration < 4 ns).

3.4.3. Reagents and materials

For the preparation of U test particles the following reagents and materials were used: uranyl nitrate ($UO_2(NO_3)_2$) (Reanal Ltd., Hungary), anion exchange resins (AG 1×8, BioRad Ltd., USA), HCl of analytical grade.

Three types of sample holders were used in this study: (1) transparent, adhesive tape (TESA, Beiersdorf, Germany), lacquer spray (Wellaflex, Germany), (2) Al sheet, adhesive carbon tape (Christine Gröpl, Germany) and (3) Al sheet, adhesive carbon tape, polycarbonate membrane with 0.4 μm pore size (Whatman, USA, Cyclpr PCH 25mm .4um or Millipore®, USA, Isopore®, VCWP 0.4), lacquer spray. The reference points on the sample holder for the localization were made from colorful paper notes (Kores, Spain).

Detachable polycarbonate filter holders (Albet, Spain, Albet-PF-25-P-12) were used as vacuum impactor heads in the procedure for micromanipulation. Tygon laboratory tubes (Saint-Gobain, USA, Tygon Laboratory tubing, R-3603) were used as a connection between the head and the membrane pump (KNF Neuberger GmbH, Germany). Different types of glues (Loctite Super Attack Power Gel, Germany and UHU Glue Stick, Germany) and micromanipulation needles (GGB Industries, INC., USA, Picoprobe needle ST-20-0.5; Mitutoyo, Japan and Bohin, France) were tested for micromanipulation purposes.

3.4.4. Samples

Test particles containing natural U as simulated ‘hot’ particles were made in order to test the procedures for the identification, localization and re-localization of particles containing alpha emitting materials and for the analysis of single particles by LA-ICP-MS. These particles were also used for the mass bias correction in the LA-ICP-MS measurements. Uranyl nitrate in 9 mol L^{-1} HCl media was loaded onto anion exchange resins to produce U test particles. Each anion exchange bead with an average diameter of 140 μm contained

approximately 13 mBq ^{238}U (approximately 1 μg U). The size of the investigated particles varied between 80 and 200 μm. The samples were labeled as M12976, M12981 and M12982.

Particles originating from confiscated nuclear fuel pellets were investigated in order to test and to validate the method for particle analysis. Particles were removed from three pellets either using swipe samples or using adhesive transparent tapes which were used afterwards as sample holders. The U in the samples had different enrichments: depleted (DU), natural (NU) and low enriched U (LEU). The size of the investigated particles varied between 8 and 400 μm.

Monazite particles originating from sand in Sri Lanka were also analyzed in order to test the procedures for the identification, the localization of particles containing alpha emitting material and the micromanipulation. The size of the investigated particles varied between 100 and 400 μm. Monazite is in fact three types of mineral with similar composition: monazite(Ce) ($(Ce,La,Nd,Th,Y)PO_4$), monazite(La) ($(La,Ce,Nd)PO_4$) and monazite(Nd) ($(Nd,La,Ce)PO_4$) [Monazite]. It can contain significant amount of Th or U.

Particles originating from the primary and secondary coolant of the Nuclear Power Plant, Paks were also analyzed in order to test the procedure for micromanipulation. In the nuclear power plant 250 mL primary coolant was filtered through a polycarbonate membrane with a pore size of 0.40 μm (Millipore® Isopore® VCWP 0.4; Millipore, USA). The membrane served as sample holder. The particles were fixed further onto the membrane using lacquer spray.

NIST 612 U containing glass reference material (NIST, USA; in the followings NIST 612) was used for optimization of the LA-ICP-MS (37.1 mg kg^{-1} ^{238}U - information value).

Highly enriched U-oxide powder from an interlaboratory exercise of Nuclear Smuggling International Technical Working Group (ITWG), 2001 was used for mass bias correction. The U-oxide powder was in form of a disk-shaped pellet (diameter: 5 mm, thickness: 1 mm) (in the followings RR HEU pellet).

3.4.5. The method for particle analysis

3.4.5.1. The sample holder

The sample holder appropriate for particle analysis has to meet several requirements. It has to be able to be used in all procedures of the developed method: the identification, the localization, the micromanipulation and the analysis by LA-ICP-MS; moreover it has to be able to be used in SEM, as well.

First of all, the sample holder - on one hand - had to be able to fix properly the particles to avoid particle loss during the sample treatment and transfer but - on the other hand - the fixation had to allow the micromanipulation of the particles of interest. Secondly, since the examination by SEM had been planned to be a possible part of the method, the sample holder had to be built up by conductive material. Finally, the size of the sample holder had to fit to different instruments (e.g. optical microscopes, SEM, LA-ICP-MS). The sample chamber of the laser ablation system (maximum size: length: 35 mm, width: 25 mm, height: 5 mm), the optical microscopes and the SEM (maximum size: length: 30 mm, width: 30 mm, height: 10 mm) was limited especially in height. Taking into account all the requirements the optimal set-up of the sample holder was the following: an adhesive carbon disk (diameter: 25 mm) was placed on an Al sheet with oxidized surface. A polycarbonate membrane (diameter: 25 mm, thickness: 20 μm) used optionally for collecting particles was fixed onto the carbon disk. The membrane was used for such an analysis where the fixation of the particles was important (e.g. microscopy, particle counting) [Millipore 2009]. For further fixation of the particles a thin layer of lacquer was applied onto the membrane. However, the lacquer layer and the polycarbonate membrane were insulator materials, their relatively small thickness still allowed the analysis by SEM. Only the quality of the SEM images were slightly affected (less sharp images could be made), the results of the energy dispersive X-ray spectrometric measurements were unaffected.

3.4.5.2. Procedure for particle removal from swipe samples

The particle removal from swipe samples was necessary to collect the particles from the original swipes onto the above mentioned, appropriate sample holder to be able to examine them. The vacuum impactor technique had been chosen for particle removal since it can transport the particles directly onto a polycarbonate membrane which is a component of the sample holder developed for the particle analysis. This technique has also an important advantage: it can be carried out in clean laboratory environment using glove box in a fume hood as it is done at the Safeguards Analytical Laboratory of the IAEA [Kuno 2008]. In this study the tests of the procedure have been carried out in analytical laboratory environment.

A plastic, detachable filter holder is used as the impactor head and it is connected to a membrane pump with a Tygon tube (Fig. 18). The polycarbonate membrane is placed into the filter holder and the particles are removed from the swipe sample using the head and the membrane pump. Afterwards the membrane is attached to the adhesive carbon disk which was previously fixed onto the Al sheet.

Fig. 18 The vacuum impactor head

The vacuum impactor technique has been tested. Inactive dust was collected with swipe samples and it was removed by the vacuum impactor. The too intensive and comprehensive particle removal can cause the overload of the membrane thus particle analysis will be impossible to perform. Therefore during the particle removal the aim is not to remove as many particles as possible but to transport particles from the swipe samples which represent the sample. The vacuum impactor is applied along three parallel lines on the swipe sample and additional three lines which are perpendicular to the previous ones. The procedure has been also tested on real samples together with the other procedures. The results will be discussed later (4.4.6. and 4.4.7.).

3.4.5.3. Procedure for the identification of particles containing alpha emitting material using solid state nuclear track detectors

After collecting the particles onto the sample holder the particles containing alpha emitting material had to be identified among the non-radioactive particles which were usually the majority of the particles in the sample.

In case of the procedure for the identification of particles containing alpha emitting material, several considerations had to be taken into account. Besides the economical issues, the procedure had to be able to fit into the method for particle analysis for safeguards purposes. This procedure had to be able to be used in case of the sample holder described in the previous chapter and it had to be able to be combined with the procedure for the localization of the particles of interest. Taking into account these requirements the use of solid state nuclear track detectors appeared to be optimal due to its relatively low price, simple usage and the fact that the identification of the particles includes the opportunity of the localization.

The developed procedure based on using nuclear track detectors can identify particles containing alpha emitting material. The procedure has three basic steps: (1) exposition (the

sample holder containing the particles is exposed to the track detectors), (2) etching to enhance the nanometer size nuclear tracks to μm size ones and (3) analysis in optical microscopes. These steps have been studied in detail and their parameters have been optimized.

During the preliminary tests for optimization of each step, transparent, adhesive tape (surface of 100 mm^2) with a plastic frame was used as sample holders for U test and monazite sand particles as test samples. (In case of the sample holder developed for the particle analysis, four nuclear track detectors had to be used to cover the surface of the membrane. Test particles were placed one by one onto the sample holder and they were fixed further by a thin lacquer layer. For the exposition the track detectors were attached to the sample holder. Several exposition times were applied (varied between 1 and 14 days). Afterwards the track detector was removed from the sample holder and rinsed with ethyl alcohol. The etching was carried out in 6.25 mol L^{-3} NaOH at 90 ± 3 ºC and different etching times were applied (varied between 2 and 4.5 h). The examination of the nuclear tracks was carried out in the optical microscope of the laser ablation system.

The particles containing alpha emitting material form a cluster (in the followings nuclear track) built up by several single tracks. The size and the shape of the clusters depend mostly on the activity and the alpha energy of the alpha emitting material besides the location of the alpha emitting material in or on the particle. The particle shape can also affect the cluster shape especially in case of low activity. Fig. 19 and Fig. 20 show examples of the nuclear tracks made by U test particles and monazite sand particles containing Th. From the cluster shape one could predict the particle shape in these cases. The exposition time was 5 days in case of the U test particles. In case of the monazite sand particles the activity of the given particles differed as it can be seen from the number of the single nuclear tracks made by the different particles (Fig. 20). Therefore a relatively long exposition time (9 days) was chosen to be able to detect particles with low activity, as well. The nuclear track sizes were usually comparable to the particle sizes, hence the particle size could be predicted. In contrary Fig. 21 shows an example of a nuclear track (exposition time: 14 days) made by a particle originating from the primary coolant of the Nuclear Power Plant, Paks. Since the particle could not be found on the sample holder in the optical microscope, it is assumed its size was less than ~2 μm. It was supposed that significantly big amount of radioactive isotopes with high specific activity was distributed mainly on the surface of the given particle.

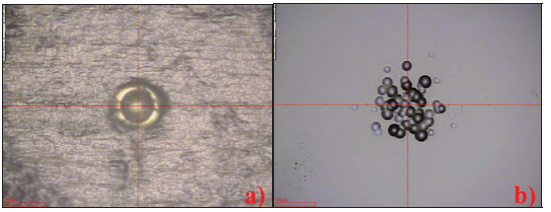

Fig. 19 A U test particle (a) and its nuclear track (b) on the nuclear track detector: the cluster is formed by single tracks

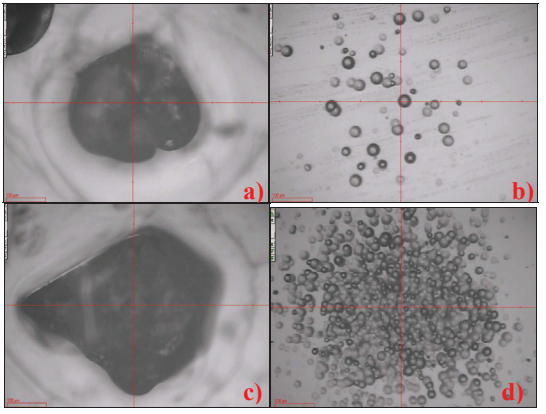

Fig. 20 Monazite sand particles containing alpha emitting material (a, c) and their nuclear tracks (b, d) on the nuclear track detector: the clusters were formed by single tracks

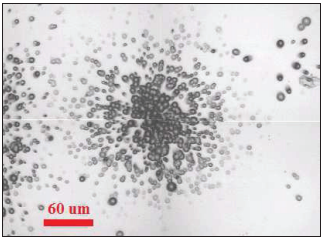

Fig. 21 Nuclear track of a particle originating from the primary coolant of the Nuclear Power Plant, Paks

The optimal exposition time depends on the amount of the alpha emitting material, the radioactive isotopes and the particle size. The exposition time is optimal if the nuclear track contains as many single tracks which helps to find its center for the localization of the identified particle. According to the experience from the identification of radioactive particles from various sources, first, the applied exposition time should be between 5 and 7 days since

this time interval was appropriate for almost all sample types which were investigated in this study. The exposition can be repeated if the nuclear tracks formed in 5-7 days are not appropriate for the localization procedure.

After the exposition the nuclear track detectors have to be etched. The standard etching procedure (in 6.25 mol L^{-1} NaOH at 90 ºC for 4.5 h) suggested by the Radosys Ltd [Radosys 2007] proved to be appropriate in the identification procedure, only the etching time was modified. The parameters found in the literature were also similar to those of the standard procedure. The etching time between 3 h 20 min and 4 h 30 min resulted appropriate single track sizes (~20 - ~40 μm) which formed such nuclear track clusters that the center of them could be easily determined.

The procedure developed is capable of identifying particles containing alpha emitting material according to the results of the preliminary tests. Using nuclear track detectors gives an excellent opportunity for the particle localization since the particles can be localized according to their nuclear tracks. The nuclear track detectors have another important advantage, namely the applied exposition time can be chosen according to the given aim: which kind of particles (low or higher activity) has to be identified. For the identification of particles containing approximately 10 mBq U 5 days of exposition time is necessary.

3.4.5.4. Procedure for the localization and relocalization of the identified particles

My objective was to establish calculation procedures which are unambiguously able to localize the previously identified particle according to its nuclear track and to relocalize it in any coordinates system. Therefore the 3- and the 6-point algorithm were chosen as the basis of the procedures.

In this chapter, first the mathematical basis of these algorithms will be discussed. Secondly, detailed descriptions will be given about the calculation procedures based on 3- and 6-point algorithms focusing on the practical details and the required information needed for the calculations. Finally, the results of the tests for the determination of the accuracy will be detailed.

3.4.5.4.1. The mathematical basis of the 3-point algorithm

Let $\boldsymbol{E}$ be a base of the n dimensional linear space, $\mathbf{R_n}$. The base vectors of $\boldsymbol{E}$ are the vectors $\mathbf{e_1}, \mathbf{e_2}, \ldots, \mathbf{e_n}$ which are linearly independent. Any vector $\mathbf{x}$ of $\mathbf{R_n}$ can be built up by the linear combination of the base vectors:

$$\mathbf{x} = \alpha_1 \mathbf{e_1} + \alpha_2 \mathbf{e_2} + ... + \alpha_n \mathbf{e_n}, \tag{17}$$

where numbers $\boldsymbol{\alpha}_1$, $\boldsymbol{\alpha}_2$, ... $\boldsymbol{\alpha}_n$ are the coordinates of the vector $\mathbf{x}$ in base $\{\mathbf{e_1}\ \mathbf{e_2}\ ...\ \mathbf{e_n}\}$. [Rózsa 1974]

In case of the transformation from a base of $\mathbf{R_n}$ to another base of $\mathbf{R_n}$, the coordinates of the vector $\mathbf{x}$ of $\mathbf{R_n}$ have to be determined in the new base according to its coordinates in the original base:

$$\mathbf{x} = \tilde{\alpha}_1 \tilde{\mathbf{e}}_1 + \tilde{\alpha}_2 \tilde{\mathbf{e}}_2 + ... + \tilde{\alpha}_n \tilde{\mathbf{e}}_n, \tag{18}$$

where numbers $\tilde{\boldsymbol{\alpha}}_1$, $\tilde{\boldsymbol{\alpha}}_2$, ... , $\tilde{\boldsymbol{\alpha}}_n$ are the coordinates of the vector $\mathbf{x}$ in base $\{\tilde{\mathbf{e}}_1\ \tilde{\mathbf{e}}_2\ ...\ \tilde{\mathbf{e}}_n\}$ [Rózsa 1974].

In the base of $\mathbf{R_n}$, in one plane there are n linearly independent reference points (A_1 ... A_n) and a P point whose vector $\mathbf{p}$ can be expressed by the vectors of reference points A_1 ... A_n (Fig. 22). The vectors of reference point A_1 ... A_n are the base vectors of the base of $\mathbf{R_n}$.

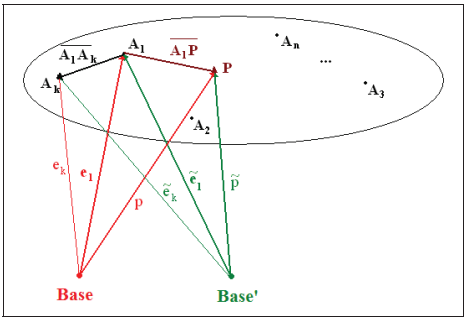

Fig. 22 General case of the 3-point algorithm in the base $\mathbf{R_n}$

The following phrases can be given in case of this system:

$$\left.\begin{aligned} A_1A_k &= \mathbf{b_k} && (19)\\ \mathbf{e_k} &= \mathbf{e_1} + \mathbf{b_k} && (20)\\ \tilde{\mathbf{e}}_k &= \tilde{\mathbf{e}}_1 + \tilde{\mathbf{b}}_k && (21) \end{aligned}\right\} \quad k = 2, 3, \ldots, n$$

Vectors $\mathbf{p}$ and $\tilde{\mathbf{p}}$ needed for the localization, can be expressed by the linear combination of the base vectors:

$$\mathbf{p} = \alpha_1 \mathbf{e_1} + \alpha_2 \mathbf{e_2} + ... + \alpha_n \mathbf{e_n} \tag{22}$$

$$\tilde{\mathbf{p}} = \tilde{\alpha}_1 \tilde{\mathbf{e}}_1 + \tilde{\alpha}_2 \tilde{\mathbf{e}}_2 + ... + \tilde{\alpha}_n \tilde{\mathbf{e}}_n \tag{23}$$

Eq. 7 and 8 can be expressed with matrices:

$$\mathbf{p} = [\mathbf{e}_1 \quad \mathbf{e}_2 \quad \ldots \quad \mathbf{e}_n] \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \ldots \\ \alpha_n \end{bmatrix} \tag{24}$$

$$\tilde{\mathbf{p}} = [\tilde{\mathbf{e}}_1 \quad \tilde{\mathbf{e}}_2 \quad \ldots \quad \tilde{\mathbf{e}}_n] \begin{bmatrix} \tilde{\alpha}_1 \\ \tilde{\alpha}_2 \\ \ldots \\ \tilde{\alpha}_n \end{bmatrix} \tag{25}$$

Eq. 22 and 23 can be expressed according to Eq. 19, 20 and 21 as the followings:

$$\mathbf{p} = \alpha_1 \mathbf{e}_1 + \sum_{k=2}^{n} \alpha_k (\mathbf{e}_1 + \mathbf{b}_k) = \mathbf{e}_1 \sum_{k=1}^{n} \alpha_1 + \sum_{k=2}^{n} \alpha_k \mathbf{b}_k \tag{26}$$

$$\tilde{\mathbf{p}} = \tilde{\alpha}_1 \tilde{\mathbf{e}}_1 + \sum_{k=2}^{n} \tilde{\alpha}_k (\tilde{\mathbf{e}}_1 + \mathbf{b}_k) = \tilde{\mathbf{e}}_1 \sum_{k=1}^{n} \tilde{\alpha}_1 + \sum_{k=2}^{n} \tilde{\alpha}_k \mathbf{b}_k \tag{27}$$

Using Eq. 17 and 18 vector $\mathbf{A_1P}$ can be expressed in both bases:

$$\mathbf{A}_1\mathbf{P} = \mathbf{p} - \mathbf{e}_1 = \tilde{\mathbf{p}} - \tilde{\mathbf{e}}_1 \tag{28}$$

$$\mathbf{A}_1\mathbf{P} = \mathbf{p} - \mathbf{e}_1 = \mathbf{e}_1 \left(\sum_{k=1}^{n} \alpha_k - 1 \right) + \sum_{k=2}^{n} \alpha_k \mathbf{b}_k \tag{29}$$

$$\mathbf{A}_1\mathbf{P} = \tilde{\mathbf{p}} - \tilde{\mathbf{e}}_1 = \tilde{\mathbf{e}}_1 \left(\sum_{k=1}^{n} \tilde{\alpha}_k - 1 \right) + \sum_{k=2}^{n} \tilde{\alpha}_k \mathbf{b}_k \tag{30}$$

$$\mathbf{e}_1 \left(\sum_{k=1}^{n} \alpha_k - 1 \right) + \sum_{k=2}^{n} \alpha_k \mathbf{b}_k = \tilde{\mathbf{e}}_1 \left(\sum_{k=1}^{n} \tilde{\alpha}_k - 1 \right) + \sum_{k=2}^{n} \tilde{\alpha}_k \mathbf{b}_k \tag{31}$$

Eq. 31 can only be fulfilled if $\sum_{k=1}^{n} \alpha_k = 1$, $\sum_{k=1}^{n} \tilde{\alpha}_k = 1$ and $\alpha_k = \tilde{\alpha}_k$, k = 1 … n. Eq. 31 has to be modified as follows to see the equality of the coordinates:

$$\mathbf{e}_1 \left(\sum_{k=1}^{n} \alpha_k - 1 \right) - \tilde{\mathbf{e}}_1 \left(\sum_{k=1}^{n} \tilde{\alpha}_k - 1 \right) = \sum_{k=2}^{n} (\tilde{\alpha}_k - \alpha_k) \mathbf{b}_k \tag{32}$$

The vectors at the right side are in the same plane since each $\mathbf{b_k}$ is in that plane. Therefore the components perpendicular to this plane of the vectors at the left side are zero. Since the two bases were chosen arbitrarily, this can only be true if $\sum_{k=1}^{n} \alpha_k = \sum_{k=1}^{n} \tilde{\alpha}_k$ which results the followings:

$$\sum_{k=2}^{n} (\tilde{\alpha}_k - \alpha_k) \mathbf{b}_k = 0 . \tag{33}$$

Since vectors $\mathbf{b_k}$ are linearly independent, the equation 17 can be true only if $\tilde{\alpha}_k - \alpha_k = 0$, k = 2, k, …, n.

According to the above assumptions Eq. 24 and 25 can be written as follows:

$$\tilde{\mathbf{p}} = [\tilde{\mathbf{e}}_1 \quad \tilde{\mathbf{e}}_2 \quad \ldots \quad \tilde{\mathbf{e}}_n][\mathbf{e}_1 \quad \mathbf{e}_2 \quad \ldots \quad \mathbf{e}_n]^{-1} \mathbf{p} \tag{34}$$

In case of the localization and the relocalization of particles, the linear space is 3 dimensional and the reference points, the tracks as well as the particles are coplanar. The reference points have to be linearly independent, so the vectors of the reference points can be base vectors.

In case of the 3-point algorithm (relocalization), let A, B and C be the reference points and P the particle and furthermore (x_1, y_1), (x_2, y_2) and (x_3, y_3) be the coordinates of the reference points A, B and C, respectively and (x_P, y_P) be the coordinates of the particle in the coordinates system of the first instrument. Let A', B' and C' be the reference points and P' the particle and furthermore $(\tilde{x}_1, \tilde{y}_1)$, $(\tilde{x}_2, \tilde{y}_2)$ and $(\tilde{x}_3, \tilde{y}_3)$ be the coordinates of the reference points A', B' and C', respectively and $(\tilde{x}_P, \tilde{y}_P)$ be the coordinates of the particle in the coordinates system of the second instrument.

The Eq. 34 is written as follows:

$$\begin{bmatrix} \tilde{x}_P \\ \tilde{y}_P \\ 1 \end{bmatrix} = \begin{bmatrix} \tilde{x}_1 & \tilde{x}_2 & \tilde{x}_3 \\ \tilde{y}_1 & \tilde{y}_2 & \tilde{y}_3 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \\ 1 & 1 & 1 \end{bmatrix}^{-1} \begin{bmatrix} x_P \\ y_P \\ 1 \end{bmatrix}. \tag{35}$$

This is the formula of 3-point algorithm.

3.4.5.4.2. The mathematical basis of the 6-point algorithm

In case of the 6-point algorithm (Fig. 25), let D_1^I, D_2^I and D_3^I be the reference points of the nuclear track detector in the first coordinates system, H_1^I, H_2^I and H_3^I be the reference points of the sample holder in the first coordinates system. Let D_1^{II}, D_2^{II} and D_3^{II} be the reference points of the nuclear track detector in the second coordinates system, H_1^{II}, H_2^{II} and H_3^{II} be the reference points of the sample holder in the second coordinates system. Let D_1^{III}, D_2^{III} and D_3^{III} be the reference points of the nuclear track detector in the third coordinates system, H_1^{II}, H_2^{II} and H_3^{II} be the reference points of the sample holder in the third coordinates system. Let T^I and T^{II} be the track in the first and the second coordinates system, respectively and let P^I and P^{III} be the particle in the first and the third coordinates system, respectively.

The following statements can be considered: In the first coordinates system, the coordinates of the nuclear track (T^I) and the particle (P^I) are the same:

$$T^I = P^I. \tag{36}$$

The coordinates of the track in the first and the second coordinates system (T^{I} and T^{II}) and the coordinates of the particle in the first and the third coordinates system (P^{I} and P^{III}) can be expressed as follows by the base matrices built up by the vectors of reference points in the certain coordinates systems considered as base vectors if the vectors of the reference points are linearly independent:

$$P^{I} = T^{I} = \begin{bmatrix} D_1^{I} & D_2^{I} & D_3^{I} \end{bmatrix} \begin{bmatrix} \boldsymbol{\alpha}_1 \\ \boldsymbol{\alpha}_2 \\ \boldsymbol{\alpha}_3 \end{bmatrix} = \begin{bmatrix} H_1^{I} & H_2^{I} & H_3^{I} \end{bmatrix} \begin{bmatrix} \tilde{\boldsymbol{\alpha}}_1 \\ \tilde{\boldsymbol{\alpha}}_2 \\ \tilde{\boldsymbol{\alpha}}_3 \end{bmatrix}, \tag{37}$$

$$T^{II} = \begin{bmatrix} D_1^{II} & D_2^{II} & D_3^{II} \end{bmatrix} \begin{bmatrix} \boldsymbol{\beta}_1 \\ \boldsymbol{\beta}_2 \\ \boldsymbol{\beta}_3 \end{bmatrix}, \tag{38}$$

$$P^{III} = \begin{bmatrix} H_1^{III} & H_2^{III} & H_3^{III} \end{bmatrix} \begin{bmatrix} \boldsymbol{\gamma}_1 \\ \boldsymbol{\gamma}_2 \\ \boldsymbol{\gamma}_3 \end{bmatrix}. \tag{39}$$

The coordinates of the track (T) can be expressed in the first coordinates system according to Eq. 35 if the second coordinates system is considered as the "original" and the first coordinates system as the "new" basis:

$$T^{I} = \begin{bmatrix} D_1^{I} & D_2^{I} & D_3^{I} \end{bmatrix} \begin{bmatrix} D_1^{II} & D_2^{II} & D_3^{II} \end{bmatrix}^{-1} T^{II}. \tag{40}$$

The coordinates system of the particle (P) can be expressed in the third coordinates system according to Eq. 35 if the first coordinates system is considered as the "original" and the third coordinates system as the "new" basis:

$$P^{III} = \begin{bmatrix} H_1^{III} & H_2^{III} & H_3^{III} \end{bmatrix} \begin{bmatrix} H_1^{I} & H_2^{I} & H_3^{I} \end{bmatrix}^{-1} P^{I}. \tag{41}$$

Since in the first coordinates system $T^{I} = P^{I}$, equation 22 can be substituted into the Eq. 41:

$$P^{III} = \begin{bmatrix} H_1^{III} & H_2^{III} & H_3^{III} \end{bmatrix} \begin{bmatrix} H_1^{I} & H_2^{I} & H_3^{I} \end{bmatrix}^{-1} \begin{bmatrix} D_1^{I} & D_2^{I} & D_3^{I} \end{bmatrix} \begin{bmatrix} D_1^{II} & D_2^{II} & D_3^{II} \end{bmatrix}^{-1} T^{II}. \tag{42}$$

This is the formula of 6-point algorithm.

3.4.5.4.3. Description of the calculation procedure based on 3-point algorithm

The calculation procedure based on 3-point algorithm (Fig. 23) can be used for the localization as well as the relocalization of particles. First of all, for the localization three-three reference points have to be placed on the sample holder and on the nuclear track detector, as well. It is essential in this case that the reference points are congruent. After the

exposure and the etching, the coordinates of the reference points and nuclear tracks generated by the particles on the nuclear track detector have to be determined by an optical microscope. Afterwards the nuclear track detector is replaced by the sample holder in the optical microscope and the coordinates of the reference points are determined. Finally, the coordinates of the particle can be calculated according to the formula of the 3-point algorithm (detailed in chapter 3.4.5.4.1.).

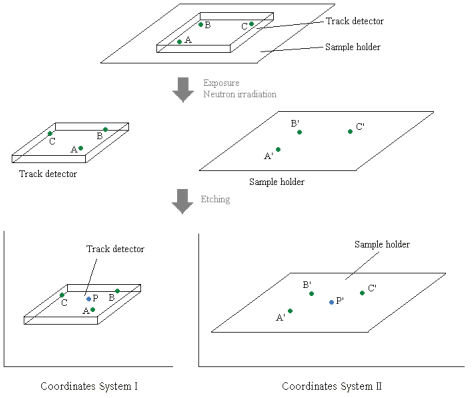

Fig. 23 The 3-point algorithm for localization

For the relocalization (Fig. 24), the coordinates of the reference points on the sample holder and those of the particles are already known in the original coordinates system (registered during the localization procedure). For further analysis the sample holder is transferred into another equipment and the coordinates of the reference points are noted in that coordinates system, as well. Afterwards the coordinates of the particle in this coordinates system can be calculated according to the formula of 3-point algorithm.

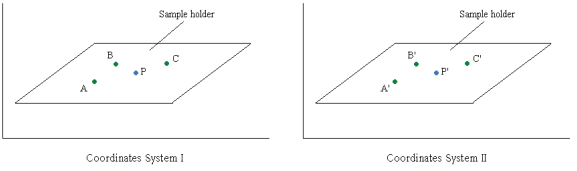

Fig. 24 The 3-point algorithm for relocalization

3.4.5.4.4. Description of the calculation procedure based on 6-point algorithm

The 6-point algorithm can be used for the localization of particles. In case of this algorithm it is not a requirement for the reference point triplets to be congruent. They are placed on the sample holder and on the nuclear track detector three dot marks are defined as reference points. After the exposure, the coordinates of the two reference point triplets are registered in the first coordinates system when the sample holder and the nuclear track detector are still fixed together to determine the location of the two triplets correlated to each other. After the separation of the sample holder and the nuclear track detector, the coordinates of the nuclear tracks originated from particles and those of the reference points are registered in the second coordinates system. Finally, in the third coordinates system, the reference points of the sample holder are noted and the coordinates of the particles are calculated according to the data from the first and the second coordinates system using the 6-point algorithm (Fig. 25).

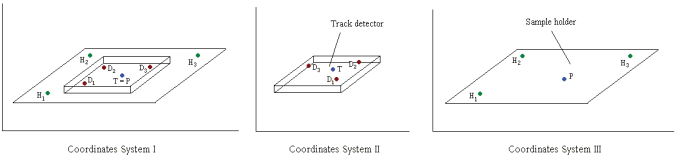

Fig. 25 The 6-point algorithm

3.4.5.4.5. Determination of the accuracy and precision of the calculation procedures

The accuracy and precision of the calculation procedures (localization and relocalization by 3-points algorithm and localization by 6-points algorithm) were tested (accuracy tests) using U test particles. They were chosen since U was assumed to be homogenously distributed in the ion exchange resin beads since they were saturated with U during the preparation and the shape of the beads can be considered as sphere. The sample holders were transparent, adhesive tapes with a shape equal to the nuclear track detectors and a transparent plastic frame. Typically 5-22 U test particles were placed onto each sample holder. For the accuracy tests of 3-point algorithm after placing the track detector, the sample holder was perforated with a tiny, sharp needle in three places (making marks on the surface of the track detector, as well) to establish the three-three congruent reference points. For the accuracy tests

of 6-point algorithm, three triangles of approximately 2 mm side length with different colors were placed onto the sample holder and three dot marks on the nuclear track detector were defined as reference points. The alpha track analysis and the localization were done as detailed above. The exposition time was 5 days and the etching time varied between 3 h 20 min and 4 h 25 min (etching time over 3 h does not affect the accuracy and the precision of the localization). The optical microscope of the LA system was used for these tests.

The coordinates of the particles were calculated and compared to their real coordinates. The bias between them (in case of the x and the y coordinates, as well) was determined. The average and the standard deviation were calculated from the individual results defined as the accuracy (average) and precision (standard deviation) of the calculation procedures.

For the accuracy test of localization by 3-point algorithm 34 particles were investigated and the localization was done 48 times. The size of the reference points on the nuclear track detectors were enlarged significantly and became too big (>300 μm) due to the etching and the reference points had an amorphous shape which made the determination of the center of the reference points ambiguous resulting in a relatively poor accuracy and precision: 19 ± 15 μm. Therefore 3-point algorithm was decided not to be used for localization. For the accuracy test of relocalization by 3-point algorithm 29 particles were investigated and the localization was done 41 times. The accuracy and precision of the relocalization turned out to be 7 ± 6 μm. For the accuracy test of the localization by 6-point algorithm 24 particles were investigated and the localization was done 46 times. In case of the reference points on the sample holders, the coordinates of the triangle centroids were calculated and used as 'virtual' reference points. According to the results the accuracy and precision were 10 ± 7 μm.

Six-point algorithm was chosen for the localization process because not only the accuracy and the precision were significantly better but in case of 3-point algorithm the alpha track analysis could be performed only once (because of the congruent reference points made by the needle) and it also had limited usability of the 3-point algorithm (only in case of thin, perforable, transparent sample holders). Three-point algorithm was chosen for relocalization.

During the accuracy tests several parameters were observed to affect the obtainable accuracy and precision: (1) In case of particles containing significant amount of alpha emitting material, the obtained alpha tracks could be much bigger than the particles. (2) If the distribution of the alpha emitting material in the particle was not homogeneous, the track center did not concur with the particle center. (3) If the alpha track cluster consisted of only a few single tracks, it was difficult to determine its center. (4) Attention had to be taken while placing the reference points onto the sample holder to avoid covering the vertices of the

triangles with the marks of the track detector. (5) The performance of the optical microscope had also effect on the accuracy and precision. Poor illumination and a non-transparent sample holder made it difficult to read the coordinates precisely. (6) Working in different coordinates systems can also decrease the accuracy of the localization.

If these parameters were taken into account, the located particle could be found around the calculated coordinates in a circle with 20 and 15 μm radius in case of localization and relocalization, respectively.

3.4.5.6. Procedure for the micromanipulation of particles

Removing particles from the original sample holder can be necessary, e.g., if the particle density is too high or single particles are to be analyzed by alpha or gamma spectrometry. It can be done by micromanipulation in an optical microscope. In this chapter procedures for micromanipulation will be described for different types of sample holders.

Uranium test particles and particles originating from the primary coolant of the Nuclear Power Plant Paks (in the followings coolant particles) were used for testing the micromanipulation procedures. Three types of sample holders were investigated: (1) adhesive, transparent tape, (2) adhesive carbon disk placed on an Al sheet and (3) polycarbonate membrane placed on an adhesive carbon disk on an Al sheet. All types were covered with a thin lacquer layer for fixing the particles. Two types of needles were used: (1) wider needles made of nickel and (2) thinner micromanipulation needles made of wolfram. In most cases glue (Loctite Super Attack Power Gel, Germany or UHU Glue Stick, Germany) were also put on the tip of the needle to pick up the particles of interest.

The basic process of micromanipulation did not depend on the applied needle, the type of the sample holder and the particles. First of all, the sample holder containing the particle was placed onto the stage of the optical microscope then the particle of interest was located. The coordinates of the particles had to be noted, especially the coordinates of the z axis. After the localization the stage had to be lowered and the micromanipulation needle (which was previously plunged into glue) was brought into focus and set into the right angle then it had to be moved out from the middle of view where it could still be seen. The stage then was raised until it reached the focus. Depending on the sensitivity of the moving systems (that of the stage and the micromanipulator), the process of picking up the particle could be done by moving either the stage or the needle. When the needle touched, it picked up the particle which was transferred onto another sample holder. If the used glue was water soluble, a drop of distilled water was placed onto new, clean sample holder (Al sheet with oxidized surface)

then the needle was inserted into the drop for couple of minutes. Afterwards the sample holder was placed under an infra lamp to evaporate the water. The particle was fixed onto the new sample holder by a thin, glue-formed-layer.

Some steps of this technique as an example can be seen in the next figure (Fig. 26). The original sample holder was a polycarbonate membrane placed on an adhesive carbon disk on an Al sheet. Water based glue (UHU) and wolfram needle were used. The process was executed as mentioned above. The single particle was analyzed by gamma spectrometry looking for the gamma lines of radioactive corrosion products. [Vajda 2011b]

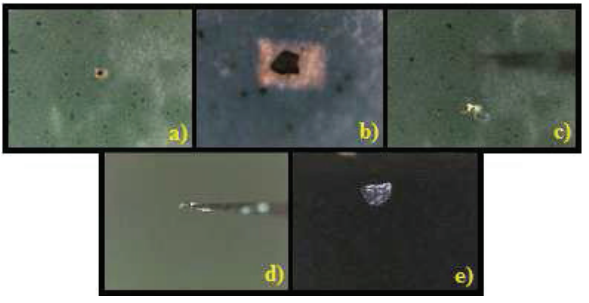

Fig. 26 Micromanipulation of a coolant particle (ID: 4-15-p5; size: 40×50 µm) using wolfram micromanipulation needle and water based glue: a) and b) the optical microscope (OM) images of the particle of interest made by the objective 10× and 50×, respectively; c) the original sample holder after the micromanipulation with the shadow of the needle; d) the particle in the glue on the needle; e) the particle on the new sample holder

Another example of the micromanipulation of a U test particle from a transparent, adhesive sample holder can be seen in Fig. 27. The size of the particle was 198 µm. The micromanipulation process was executed as mentioned above using Loctite glue. Afterwards the particle was transferred onto an adhesive carbon disk which was placed on an Al sheet. The single particle was analyzed by LA-ICP-MS.

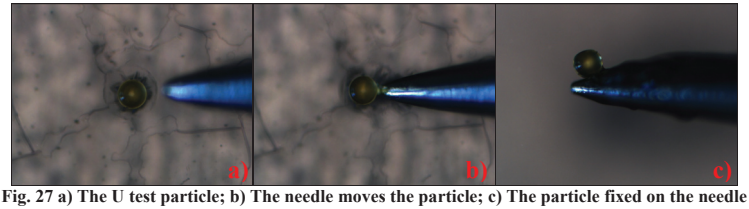

Fig. 27 a) The U test particle; b) The needle moves the particle; c) The particle fixed on the needle

The micromanipulation of a coolant particle (particle ID: 40TV0604-mp9; size: 25 µm × 40 µm) from a sample holder (Millipore® polycarbonate membrane) with high particle density

can be seen in Fig. 28-32. The particle of interest (in the white circle in Fig. 28a) was removed by wolfram needle without using any glue. It sticked onto the needle by electrostatic force. Due to the high particle density not only the particle of interest was picked up but some other particles, as well (see Fig. 31). The particle was further analyzed by SEM and gamma spectrometry. [Vajda 2009b]

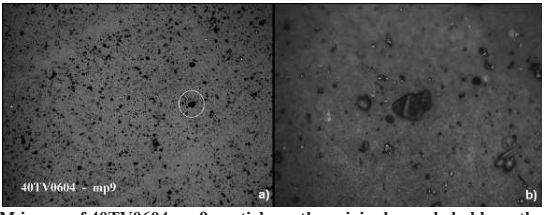

Fig. 28 The OM image of 40TV0604-mp9 particle on the original sample holder – the pictures were made by the objective 10× (a) and 50× (b)

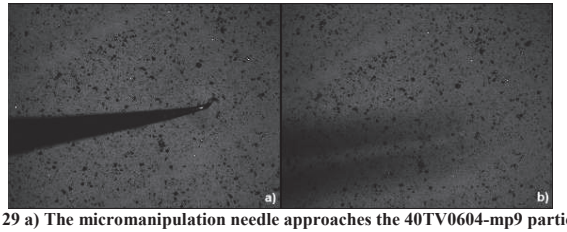

Fig. 29 a) The micromanipulation needle approaches the 40TV0604-mp9 particle; b) The original sample holder without the 40TV0604-mp9 particle

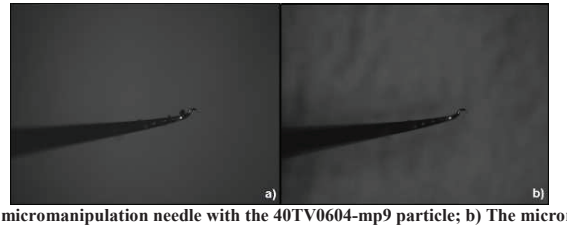

Fig. 30 a) The micromanipulation needle with the 40TV0604-mp9 particle; b) The micromanipulation needle after the 40TV0604-mp9 particle was transferred onto the new sample holder

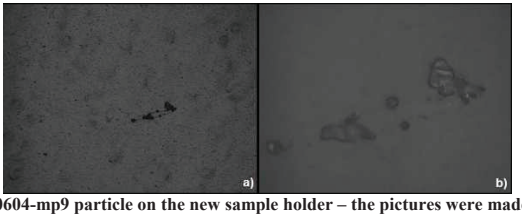

Fig. 31 The 40TV0604-mp9 particle on the new sample holder – the pictures were made by the objective 10× (a) and 50× (b)

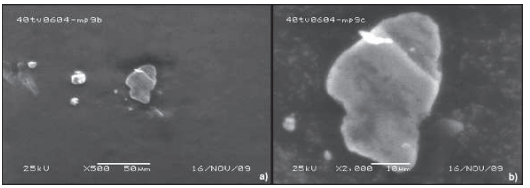

Fig. 32 The SEM image of the 40TV0604-mp9 particle magnification of the pictures are a) 500×; b) 2000×

3.4.5.7. Procedure for the analysis of single particles by LA-ICP-MS

A procedure has been developed for the determination of the U isotopic composition by LA-ICP-MS which became the final step of the analysis of single particles for safeguards purposes. The technique of LA-ICP-MS allowed only qualitative measurements and the determination of the U isotope ratios of the single particles. Quantitative measurements could not be performed due to the lack of the matrix matched standard.

The particle of interest was ablated by the laser beam and the ablated sample was introduced into the ICP-MS where the intensities of the U isotopes were measured. Low laser energy (typically less than 0.05 J cm^{-2}; < 50% (dimension of the laser energy in the LA software)) was applied to be able to achieve relatively steady signals for the U isotopes on logarithmic scale. Due to the low laser energy in most cases (typically if the particle size was bigger than 5-10 µm) only a part of the particle was ablated which is performed at the centre of the particle and the laser ablation measurements could be repeated several times.

The laser ablation parameters (ablation type, laser beam / spot size diameter, laser energy flux [mJ cm^{-2}, %], repetition rate [Hz]) were optimized during the method development. For particle analysis spot ablation was the optimal ablation type and the optimal repetition rate was 10 Hz. The laser beam / spot size diameter and the laser energy flux depended on the sample size and type as well as the U content of the particles. The laser beam / spot size diameter had to be comparable to the particle size in case of particle with a size less than approximately 60 µm. Particles bigger than 60 µm were ablated using 60 µm laser beam / spot size diameter. In this study the following laser beam diameters were used: 12, 20, 30, 40 and 60 µm. The laser energy flux was usually higher if higher laser beam / spot size diameter was used and the U content of the particle was lower. In this study the laser energy flux varied between 0.008 and 0.04 mJ cm^{-2} (30-50%). The following table (Table 18) gives some

examples of the optimal laser ablation parameters in case of different sample types and particle sizes.

Table 18 Applied laser ablation parameters in case of different particles

Particle type	Particle size	Laser beam diameter	Laser energy*
U test particle	160 µm	60 µm	40%
U test particle	160 µm	40 µm	40%
Pellet particle - LEU	10 µm × 11 µm	12 µm	40%
Pellet particle - LEU	19 µm × 34 µm	20 µm	45%
Pellet particle - LEU	40 µm × 70 µm	30 µm	45%
Pellet particle - DU	6.1 µm × 9.9 µm	20 µm	35%
Pellet particle - DU	31 µm × 54 µm	40 µm	40%
Pellet particle - DU	150 µm × 170 µm	60 µm	45%

* The laser energy is given in % in the software of the laser ablation system.
E.g. 12 µm laser beam with 40% laser energy is equal to 0.02 J cm^{-2} energy flux.

First of all, the LA-ICP-MS system was optimized using the NIST 612 reference material with respect to maximum $^{238}U^{+}$ intensity and good precision. The achieved sensitivity was typically approximately 10^5 cps for 37.1 mg kg^{-1} ^{238}U. Laser ablation parameters used for the optimization were: line scan, laser beam diameter: 60 µm, laser energy flux: ~0.10 mJ cm^{-2} (70%) and repetition rate: 10 Hz. In this study low (R = 300) and medium (R = 4000) mass resolutions were also applied. An example of the optimized operating parameters of the ICP-MS is detailed in Table 19.

Table 19 Optimized ICP-MS parameters

	Optimized operating parameters of the ICP-MS
RF power [W]	1390
Cooling gas flow rate [l min^{-1}]	16.04
Nebulizer gas flow rate [l min^{-1}]	1.096
Auxiliary gas flow rate [l min^{-1}]	1.23
Runs and passes	1×80
Mass / Search / Integration Window [%]	80 / 60 / 80
Samples per peak	20
Mass resolution	300 and 4000
Measured isotopes	^{234}U, ^{235}U, ^{236}U, ^{238}U

For the ICP-MS measurement the instrumental mass bias had to be also taken into account. For the mass bias correction the $^{235}U/^{238}U$ ratio of the RR HEU pellet or that of the U test particles containing natural U was used. The following laser ablation parameters were typically used for the mass bias correction: laser beam diameter: 60 µm, laser energy flux: ~0.10 mJ cm^{-2} (70%), repetition rate: 10 Hz. Line scan was used in case of the HEU pellet and spot scan in case of the U test particles.

Either the RR HEU pellet or a U test particle (depending on which one is used for mass bias correction) was analyzed as standard sample (1) to check the correction of the measured-calculated U isotope ratios and (2) to select the algorithm for mass bias correction (linear, exponential and power law function) [Yang 2003]. Reference values in mass percent for the RR HEU pellet were: ^{234}U/U - 0.964% ± 0.055%; ^{235}U/U - 89.475% ± 1.140%; ^{236}U/U - 0.661% ± 0.039%; ^{238}U/U - 8.906% ± 0.250% [Stefánka 2008]. In case of the U test particles the values of the isotopic composition of the natural U recommended by the IUPAC (International Union of Pure and Applied Chemistry) were used as reference values (Table 20).

The intensities of the U isotopes were recorded in the chromatographic mode of the ICP-MS during the laser ablation of the particle of interest. The background level (gas blank) was always measured in 20-25 measuring points by starting the record of the U isotope signals prior to starting the laser ablation in case of each measurement. An example of the recorded signals of the U isotopes can be seen in Fig. 33. The U isotope ratios (^{235}U/^{238}U, ^{234}U/^{238}U, ^{236}U/^{238}U) were calculated after background correction, then mass bias was corrected using the previously chosen algorithm. Finally, the U isotopic composition (the mass ratio of one isotope relative to the sum of all isotopes of the element) of the particles was evaluated. The results could be given in isotope ratios, atom or mass percent. The uncertainty of the results was calculated according to the law of the uncertainty propagation.

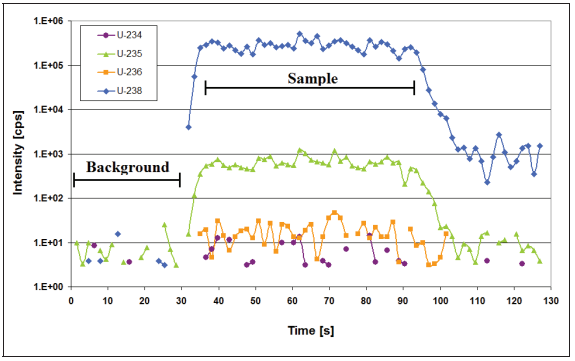

Fig. 33 The U isotope signals of a DU pellet particle (9×18 µm)

3.4.6. Analysis of the U test samples

Uranium test particles were analyzed to test the capability of each procedure of the method for particle analysis and the feasibility of the combination of these procedures. The procedure for particle removal was tested separately. The procedures for the identification, the localization/relocalization and the determination of the U isotopic composition by LA-ICP-MS were tested simultaneously. In this chapter, the analysis of U test particles is described in detail.

3.4.6.1. Testing the procedure for particle removal

Uranium test particles were placed on two swipe samples and the procedures for particle removal and for particle identification described in chapter 3.4.5.2. and 3.4.5.3., respectively, were applied. The nuclear track detectors were screened looking for nuclear tracks of the transferred U test particles. Many nuclear tracks could be found on them which prove the capability of the procedure for particle removal. The exact numbers of the particles were not determined since the aim of this procedure is not to remove as many particles as possible.

3.4.6.2. Testing the combination of the procedures of the method for particle analysis

Three U test samples (M12976, M12981 and M12982) of natural uranium composition were analyzed in order to test the feasibility of the combination of the procedures for identification, localization/relocalization and the determination of the U isotopic composition. Moreover in the analysis of the sample M12976, some parameters of the LA-ICP-MS analysis (the applied resolution of the ICP-MS, the parameters of the laser ablation and the calculation method for the U isotopic composition determination) were examined and optimized. In the analysis of the sample M12981, two calculation methods were tested. In the analysis of the sample M12982 one particle was micromanipulated prior to its U isotopic composition determination.

3.4.6.2.1. Measurement conditions

A transparent, adhesive tape sample holder (10 mm × 10 mm) was prepared and several U test particles (size: 84-196 μm) (12, 5 and 5 in case of M12976, M12981 and M12982, respectively) and three reference points were placed on it. The sample holder was coated with a thin layer of lacquer. The procedures for particle identification and for localization using 6-point algorithm described in chapter 3.4.5.3. and 3.4.5.4.2., respectively, were applied. A

nuclear track detector was placed onto the sample holder after the lacquer dried. The coordinates of the reference points of the sample holder and those of the nuclear track detector were determined during the exposition. The exposition time was 5 days. Afterwards the nuclear track detectors were etched according to the standard procedure described in chapter 3.4.5.3. The etching time was 4 h 25 min. The localization was done by the 6-point algorithm in the optical microscope of the laser ablation system.

In case of the sample M12982 the micromanipulation of a selected particle was executed under the Zeiss microscope using the Mitutoyo micromanipulator. The particle was transferred onto an adhesive carbon disk placed onto an Al sheet.

After the localization and in case of M12982 after the micromanipulation, the U isotopic composition of some particles were determined by LA-ICP-MS applying the procedure described in chapter 3.4.5.7. The optimization of the LA-ICP-MS system was followed by the measurement of the U test particles. In case of M12976 3 and 5 particles were measured in low and medium resolution, respectively to determine the optimal resolution for the method for particle analysis. In case of M12981 the U isotopic composition of each particle was determined. Three parallel measurements were executed in case of three particles. Two types of 'raw results handling' method were also tested. In case of the sample M12982 only one particle (M12982-4) was measured. The results were compared to the isotopic composition of the natural U recommended by the IUPAC (Table 20). Finally, the 'standard' sample for the determination of mass bias correction factor was measured. In case of M12976, the NIST 612 glass and the RR HEU pellet were investigated to determine which sample is more appropriate for mass bias calibration and two types of algorithm (linear and exponential) for mass bias correction were also tested. These measurements were executed in low and medium resolutions, as well. In case of the other samples, only one 'standard' sample (RR HEU pellet) was measured in one resolution (medium).

Table 20 The isotopic composition of the natural U recommended by the IUPAC was used as reference values in the analysis of U test particles

	Reference values			
	[Atom%]	±	STD	STDrel
^{234}U/U	0.0055	±	0.0005	9.1%
^{235}U/U	0.7200	±	0.0012	0.2%
^{238}U/U	99.275	±	0.006	0.01%

3.4.6.2.2. Results of the analysis of the sample M12976

The identification and the localization of the U test particles were successful, since all the 12 nuclear tracks were found on the nuclear track detector and all the 12 particles could be localized. The calculated coordinates of the particles were typically 1-30 μm far from the exact center.

Low (LR) and medium (MR) resolution were applied in case of 3 and 5 particles, respectively. The following table shows the average results. The results obtained by the measurements carried out in medium resolution mode agreed well with the reference values in contrary the results obtained by measurements carried out in low resolution mode (compare with values in Table 20). For mass bias correction the use of RR HEU pellet and the exponential algorithm proved to be more appropriate since the results using them agreed better with the reference values. In Table 21 the results were calculated using the RR HEU pellet as 'standard sample' and the exponential algorithm.

Table 21 The U isotopic composition of the U test particles from sample M12976 obtained by the results of measurements carried out in low and medium resolution modes, respectively

Isotopes	M12976 - Low Resolution Average (n = 3)				M12976 - Medium Resolution Average (n = 5)			
	[Atom%]	±	2*STD	STDrel	[Atom%]	±	2*STD	STDrel
^{234}U/U	0.0061	±	0.0004	6.2%	0.0056	±	0.0005	8.4%
^{235}U/U	0.798	±	0.012	1.4%	0.730	±	0.026	3.6%
^{238}U/U	99.196	±	0.012	0.01%	99.265	±	0.026	0.03%

3.4.6.2.3. Results of the analysis of the sample M12981

The identification and the localization of the U test particles were successful, since all the 5 nuclear tracks were found on the nuclear track detector and all the 5 particles could be localized. The calculated coordinates of the particles were typically 2-21 μm far from the exact center.

After the localization the U isotopic composition of each particle was determined by LA-ICP-MS. The background signals of the ICP-MS were collected for approximately 30 s prior to the start of the laser ablation. Each ablation took approximately 40-50 s. The intensities of the U isotopes were recorded during the ablation. Fig. 34 shows an example of the U isotope intensities collected during the measurement of a U test particle of the sample M12981. Three particles were measured three times and two particles only once.

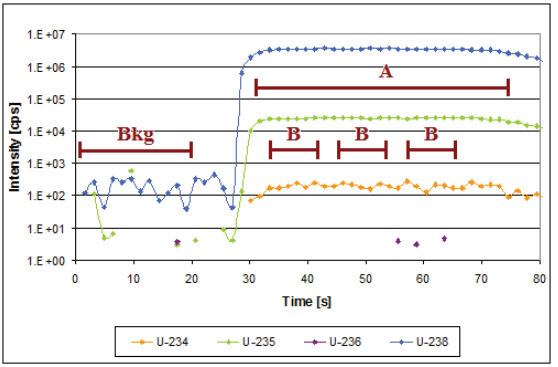

Fig. 34 The U isotope signals of a particle from the sample M12981

Two practices for handling raw results were tested. In both cases the background is calculated composing the average of the intensities recorded typically in the first 20 s (indicated with 'Bkg' in Fig. 34). The first type can be used if at least three repeated measurements can be done on the same particle. The average of the intensities of each U isotope is calculated in three time intervals (one of them is labeled by A in Fig. 34) where the signals are more or less constant in logarithmic scale. The mass bias corrected isotope ratios and the isotopic composition in atom and/or mass percent are calculated separately for all three measurement. Finally, the average and the standard deviation are composed from them. The second type of 'raw results handling' method can be used if the given particle can be measured only once and the constant part of the intensity curve contains at least 15 measuring points. Three time intervals (indicated with 'B' in Fig. 34) containing 5-5 measuring points are chosen and the isotope ratios are calculated. The average and the standard deviation are calculated prior to the mass bias correction. Finally, the mass bias corrected isotope ratios and U isotopic composition in atom and/or mass percent are calculated and the uncertainty is determined according to the law of uncertainty propagation.

There is no significant difference between the results obtained by the two calculation methods (Table 22). The values and the uncertainties are also comparable but it has to be noted that the intensity signals of each isotope were relatively high. The obtained results agreed well with the reference values (compare with values in Table 20). If a particle can be measured at least 3 times, it is recommended to apply both calculation methods to enhance the reliability of the results.

Table 22 The average U isotopic composition of the particles from sample M12981 using different types of calculation methods

	M12981 - Type A Average (n = 3)				M12981 - Type B Average (n = 10)			
	[Atom%]	±	2STD	STDrel	[Atom%]	±	2STD	STDrel
$^{234}U/U$	0.0056	±	0.0001	2.4%	0.0056	±	0.0003	5.4%
$^{235}U/U$	0.740	±	0.018	2.5%	0.736	±	0.013	1.7%
$^{238}U/U$	99.254	±	0.019	0.02%	99.259	±	0.013	0.01%

3.4.6.2.4. Results of the analysis of the sample M12982

The identification and the localization of the U test particles were successful, since all the 5 nuclear tracks were found on the nuclear track detector and all the 5 particles could be localized. The calculated coordinates of the particles were typically 5-35 μm far from the exact center.

Since the localization and the micromanipulation were not executed at the same time and place, relocalization had to be done using the results of the localization and the 3-point algorithm. The accuracy and precision of the calculated coordinates were not changed (the typical differences between the calculated coordinates and the exact centers were 5-39 μm) carrying out the relocalization in two different equipment (the optical microscope of the LA system and the Zeiss microscope).

A randomly selected particle, namely M12982-4 was micromanipulated under the Zeiss microscope and transferred onto a carbon disk. The U isotopic composition of the particle was determined by LA-ICP-MS. The particle was measured 3 times and the average results can be seen in Table 23 which agreed well with the reference values (compare with values in Table 20).

Table 23 The U isotopic composition of the micromanipulated particle originating from the sample M12982

	M12982-4 Average (n = 3)			
	[Atom%]	±	STD	STDrel
$^{234}U/U$	0.0057	±	0.0007	11.4%
$^{235}U/U$	0.74	±	0.03	3.5%
$^{238}U/U$	99.26	±	0.03	0.03%

3.4.7. Validation - Analysis of particles originating from confiscated nuclear fuel pellets

3.4.7.1. Measurement conditions

Swipe samples were taken from the surface of three confiscated nuclear fuel pellets containing U with different enrichments: depleted (DU), natural (NU) and low enriched U (LEU). The particles were transferred onto a sample holder applying the procedure for particle removal described in chapter 3.4.5.2. The identification of particles containing alpha emitting material was carried out using four nuclear track detectors (exposition time: 4 days) according to the procedure described in chapter 3.4.5.3. The 6-point algorithm was used for the localization of the particles. In some cases the particles had to be relocalized since the localization and the LA-ICP-MS measurement were done on different days

The U isotopic composition of the localized particles was determined by LA-ICP-MS. The procedure applied is described in detail in chapter 3.4.5.7. After the optimization of the LA-ICP-MS system the particles of interest were measured. Parallel measurements were tried to carry out. Afterwards a U test particle was measured three times for the mass bias correction. Finally, the RR HEU pellet was measured three times as a control sample in order to check if the correct U isotopic composition can be obtained. The U isotopic composition of the particles originating from the nuclear fuel pellets were compared to the results of a joint analysis project involving the JRC Institute of Transuranium Elements (ITU) and the Institute of Isotopes (IKI). [Stefánka 2008, Stefánka 2007] These values were considered as reference values (Table 24).

Table 24 The reference values of the DU, NU and LEU pellets [Stefánka 2008, Stefánka 2007]

	DU Reference values				NU Reference values				LEU Reference values			
	[Mass%]	±	STD	STDrel	[Mass%]	±	STD	STDrel	[Mass%]	±	STD	STDrel
$^{234}U/U$	0.0012	±	0.0003	22%	0.0053	±	0.0002	3%	0.035	±	0.001	2.9%
$^{235}U/U$	0.2553	±	0.0001	0.05%	0.7107	±	0.0011	0.2%	2.517	±	0.005	0.2%
$^{236}U/U$	0.006	±	0.004	71%		-			0.45	±	0.02	4.9%
$^{238}U/U$	99.738	±	0.001	0.001%	99.284	±	0.001	0.001%	96.982	±	0.007	0.007%

3.4.7.2. Results and discussions

The particle removal, the identification and the localization were successful. Many particles could be identified and localized from the three sample holders. The particle size

varied between 8 and 400 µm. Fig. 35 shows some identified particles with their nuclear tracks. The nuclear track size was comparable to the particle size.

In the LA-ICP-MS analysis, the background signals were collected for approximately 30 s prior to the start of the laser ablation in case of each measurement. The intensities of the U isotopes were collected for approximately 40-60 s during the laser ablation. Fig. 36 shows an example of the registered intensities of the U isotopes of a given particle from each sample. The size of the particles in the examples was similar and the same laser parameters were used. It can be assumed that the U content of the DU particles is significantly less than that of the NU and LEU particles since the ^{235}U and the ^{238}U signal was smaller with approximately 1.5-2 orders of magnitude and the specific activities of the pellet particles with different enrichment were in the same order of magnitude (taking into account only the ^{235}U and the ^{238}U 12.6 Bq, 12.9 Bq and 14.1 Bq U in 1 mg of sample of the DU, NU and LEU pellets, respectively).

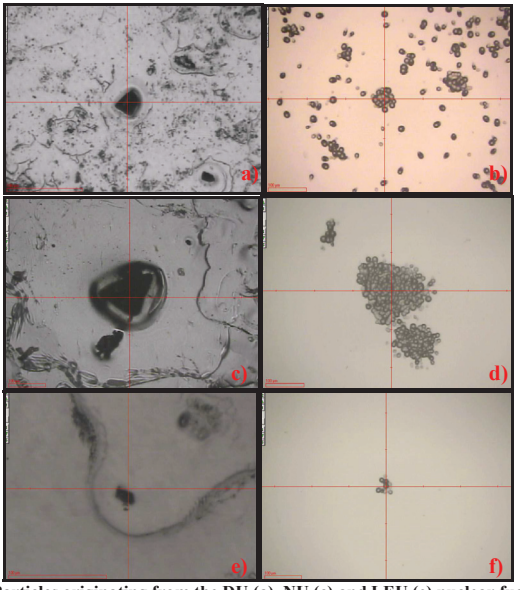

Fig. 35 Particles originating from the DU (a), NU (c) and LEU (e) nuclear fuel pellets and their nuclear tracks (signed by the cross-hair) (b, d, f)

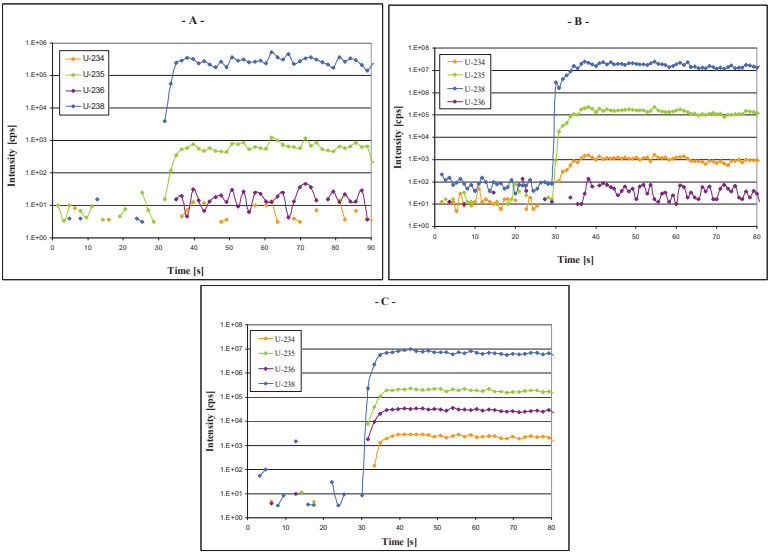

Fig. 36 The U isotope signals of DU (A), NU (B) and LEU (C) particles

The summarized results - given in mass percent similarly to the reference values - can be seen in Table 25 which are generally in good agreement with the reference values (Table 24). Some of the individual results with 2σ standard deviation did not agree with the reference values. These particles were typically smaller than 20 μm, however, disagreement also occurred in case of large particles (> 20 μm) mainly among DU particles. It was noticed that this happened mainly if samples with different enrichments had been analyzed on the day of the given measurement especially in case of particles with low U content (which was assumed from the values of the intensity signals). It is likely that the memory effect of the ICP-MS caused mainly these disagreements besides the low intensity signals resulting unreliable results.

Table 25 The U isotopic composition of the particles originating from the sample M12982

	DU Average (n = 8)				NU Average (n = 10)				LEU Average (n = 40)			
	[Mass%]	±	2*STD	STDrel	[Mass%]	±	2*STD	STDrel	[Mass%]	±	2*STD	STDrel
^{234}U/U	0.0014	±	0.0008	54%	0.0050	±	0.0002	3.6%	0.034	±	0.002	8.3%
^{235}U/U	0.26	±	0.04	14%	0.71	±	0.03	3.9%	2.56	±	0.06	5.0%
^{236}U/U	<0.006*				<0.0003*				0.42	±	0.01	5.4%
^{238}U/U	99.74	±	0.04	0.04%	99.29	±	0.03	0.03%	96.98	±	0.07	0.1%

* estimated values of LD

During the laser ablation the chosen laser beam and particle size were similar to each other and the laser beam was directed onto the center of the particle. Due to the low laser energy most of the times a second and a third measurement could be carried out even in case of 10-15 µm particles. Fig. 37 shows the U isotope signals of the first and the third measurement of a 28×50 µm LEU particle. The used laser ablation parameters (laser beam diameter: 30 µm, laser energy: 40% and repetition rate: 10 Hz) were the same in case of the 3 measurements and the intensities dropped approximately 0.5-1 order of magnitude after 3 measurements which was still enough to obtain reliable results. The uncertainties did not show significant increase.

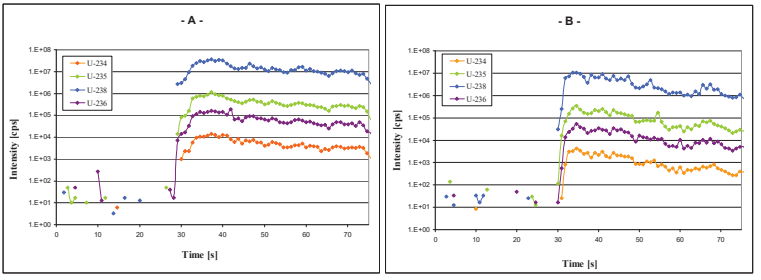

Fig. 37 The U isotope signals of LEU particle (28×52 µm) obtained by the first (A) and the third (B) LA-ICP-MS measurement (The inclination of the curves appeared due to the mass losses of the particle)

The complex method was successfully validated by the determination of the U isotopic composition of particles with known U composition originating from nuclear fuel pellets, since the particles were successfully removed from the swipe samples and identified, localized and relocalized on the developed sample holder, moreover the results obtained by the LA-ICP-MS measurements agreed well with the reference values.

It can be concluded that particles with a diameter higher than 10 µm can be analyzed by the procedure for the determination of the U isotopic composition of single particles by LA-ICP-MS. The size limitation of the procedure is originating from the fact that the measurement is executed under the optical microscope of the laser ablation system. Due to the relatively poor illumination of the optical microscope used and the dark particles on dark surface the particles could be identified with acceptable probability only above approximately 10 µm size. A spherical nuclear fuel pellet ($\rho(UO_2)$ = 10.97 g cm^{-3}; 88% U content) particle with a diameter 10 µm contains approximately 5.1 ng U which can be considered as the theoretical detection limit of this procedure although the detection limit of the LA-ICP-MS technique is in the level of 0.1 µg g^{-1} and 0.1 ng g^{-1} (the absolute detection limit is in the level

of fg-pg). [Becker 2002]. Even 1 μm size particles (containing approximately 5 pg U) could be analyzed if the limitation would be only the detection limit of the LA-ICP-MS technique.

3.4.8. Conclusions

A complex method for the determination of the U isotopic composition of single particles originating from safeguards swipe samples has been developed which offers procedures for many possible and desired steps of particle analysis beyond the methods available in the literature: procedures for (1) particle removal from swipe samples using vacuum-impactor technique, (2) the identification of particles containing alpha emitting and fissile material using solid state nuclear track detectors, (3) the precise localization and relocalization of identified particles, (4) the micromanipulation of particles and (5) the determination of the U isotopic composition of single particles (>10 μm) by LA-ICP-MS. These procedures can be further combined with the analysis by SEM, alpha and gamma spectrometry due to the sample holder developed.

The procedures separately and the feasibility of the combination of them have been tested and validated analyzing U test particles and particles originating from nuclear fuel pellets with known U isotopic composition. The obtained results were in good agreement with the reference values.

This method can be used not only in the particle analysis for safeguards purposes but e.g. in the analysis of particles originating from the primary and the secondary coolant of nuclear power plants [Vajda 2010, Vajda 2011b].

4. Summary

During my Ph.D. studies my objectives were to develop radioanalytical methods for bulk and particle analysis of safeguards swipe samples to determine the actinides in the whole sample or in radioactive particles originating from swipes using alpha spectrometry and ICP-MS. The current dissertation shows these methods and the most important results.

First of all the adaptation of a radiochemical separation method is described developed for the determination of actinides in safeguards swipe samples. The method was comprehensively tested to determine its performance parameters (detection limits of actinides, typical recoveries, and 'goodness' of separation). Real samples taken during national safeguards inspections of the Hungarian nuclear facilities were analyzed. The results proved that the method can be effectively used for safeguards purposes.

Secondly the improvement of the above method is discussed. The improved radioanalytical procedure is capable of the determination of Th, U, Np, Pu and Am(Cm) using a single TRU extraction chromatographic column in different sample types (swipe, sediment) using alpha spectrometry and ICP-MS. More information and more reliable results can be obtained using two independent measurement techniques on one sample.

Thirdly the modification of the standard procedure of the IAEA's Clean Laboratory for the determination of U and Pu content of environmental samples is shown. The modified method allows determining low level ^{238}Pu in safeguards environmental samples by alpha spectrometry using ICP-MS results of ^{239}Pu and ^{240}Pu while its original purpose can still be achieved. The accuracy and the precision of ^{238}Pu determination have been tested by the analysis of test samples. Real safeguards inspection samples were used to demonstrate the capability of the modified method.

Finally, each procedure of the complex method developed for the determination of U isotopic composition of single particles originating from safeguards swipe samples is also described: procedures for (1) particle removal from swipe samples using vacuum-impactor technique, (2) the identification of particles containing alpha emitting material using solid state nuclear track detectors, (3) the precise localization and relocalization of identified particles, (4) the micromanipulation of particles and (5) the determination of the U isotopic composition of single particles by LA-ICP-MS. These procedures separately and the feasibility of the combination of them were tested and validated analyzing U test particles and particles originating from nuclear fuel pellets with known U composition.

5. Összefoglalás

A doktori munkám során safeguards dörzsminták tömbi és részecske-analízisére alkalmas radioanalitikai módszereket fejlesztettem, melyekkel meghatározható a teljes minta vagy a mintából származó radioaktív részecskék aktinidatartalma alfa-spektrometria és ICP-MS alkalmazásával. Jelen disszertáció ezeket a módszereket és a legfontosabb eredményeket mutatja be.

Az elsőként bemutatott módszer egy radiokémiai elválasztási eljárás módostása, mely lehetővé teszi safeguards dörzsmintákban Th, U, Pu és Am(Cm) meghatározását. A módszer átfogó tesztelése során meghatároztam a teljesítmény tényezőit (kimutatási határ, elérhető, tipikus kitermelések és az elválasztás jósága). Hazai safeguards ellenőrzés során gyűjtött, valódi minták elemzésével igazoltam, hogy a módszer hatékonyan alkalmazható safeguards célokra.

A vizsgálatok során felmerült a fenti módszer továbbfejlesztésének szükségessége. Az új, továbbfejlesztett eljárás Th, U, Np, Pu és Am(Cm) meghatározására alkalmas különböző típusú mintákban (dörzsminta, üledék), melynek különlegessége, hogy az aktinidák elválasztása egyetlen TRU extrakciós kromatográfiás gyantán történik. Ezen túlmenően az alfa-spektrometria és az ICP-MS együttes alkalmazásának köszönhetően nemcsak a meghatározható izotópok köre bővült, de az eredmények megbízhatósága is javult.

A Nemzetközi Atomenergia Ügynökség (NAÜ) Tiszta Laboratóriumában környezeti minták U- és Pu-tartalmának meghatározására alkalmazott standard módszer módosítása lehetővé tette safeguards mintákban fg mennyiségű ^{238}Pu meghatározását alfa-spektrometriával és az ICP-MS eredmények (^{239}Pu és ^{240}Pu) felhasználásával. Tesztminták elemzésével megállapítottam a ^{238}Pu meghatározásának pontosságát és precizitását. Valódi, safeguards ellenőrzésből származó minták elemzésével demonstráltam a módosított módszer teljesítőképességét.

A safeguards dörzsmintákról származó egyedi részecskék U izotópösszetételének meghatározására alkalmas módszer számos, egymáshoz jól illeszthető és egymással kombinálható eljárásból épül fel: (1) a részecskék dörzsmintákról vákuum-impaktorral történő eltávolítása, (2) szilárdtest nyomdetektorok alkalmazásával alfasugárzó anyagot tartalmazó, egyedi részecskék azonosítása, (3) az azonosított részecskék lokalizációja és relokalizációja, (4) a részecskék mikromanipulációja és (5) a részecskék U izotópösszetételének meghatározása LA-ICP-MS módszerrel. Az egyedi eljárásokat külön-külön és különböző kombinációkban is teszteltem és validáltam U tartalmú tesztrészecskék, valamint ismert összetételű üzemanyagpasztillákról származó részecskék elemzésével.

6. Novel contributions

1. I have successfully adapted a combined radioanalytical method - originally designed for the analysis of small environmental samples - for the determination of actinides in safeguards swipe samples. The following isotopes can be determined by the method based on alpha spectrometry: ^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{242}Cm and ^{243,244}Cm. The achieved detection limits were as low as 0.2 and 7.2 mBq/sample (in case of counting times of 20 000 and 150 000 s), and the typical recoveries were 77% ± 5%, 67% ± 12%, 51% ± 16% and 73% ± 7% for Am, Pu, Th and U, respectively. I have demonstrated the effectiveness and the capability of the method for safeguards purposes by analyzing swipe samples taken during national safeguards inspections in several Hungarian nuclear facilities.

2. I have improved the above mentioned radioanalytical method. The new method is capable of the simultaneous separation of the major and minor actinides (Th, U, Np, Pu, Am(Cm)) on a single TRU extraction chromatographic column based on selective, on-column oxidation state adjustment of actinides. The method comprises the combination of two measurement techniques, i.e., alpha spectrometry and ICP-MS, therefore the list of nuclides that can be determined has been extended and it covers ^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, (^{236}U), ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am, ^{242}Cm, ^{243}Cm and ^{244}Cm nuclides, furthermore the reliability of results has been increased. The achieved detection limits were as low as 0.001, 0.004, 0.6, 0.4 and 0.5 mBq g^{-1} for ^{235}U (ICP-MS), ^{238}U (ICP-MS), ^{238}Pu (alpha spectrometry), ^{239}Pu (ICP-MS) and ^{241}Am (alpha spectrometry), respectively. The typical recoveries of each actinide were above 50% which can be regarded as good in case of a combined radioanalytical procedure.

3. I have proved that on-column oxidation state adjustment of Np is possible on the TRU extraction chromatographic column only in case of certain oxidation states. I have proved that tetravalent Np can be oxidized to Np(VI) with Ti(IV), hexavalent Np can be reduced to Np(IV) with Ti(III) at a relatively high Ti concentration (>0.05 mol l^{-1}), and Np cannot be adjusted on-column to tri- and pentavalent oxidation states with any examined redox reagents ($K_2S_2O_5$, $NaSO_3$, $TiCl_3$; $KMnO_4$, $NaNO_2$, $K_2S_2O_8$, $K_2Cr_2O_7$ and $TiCl_4$). Moreover, I proved that Ti - as an analogue of Th - improved the elution of tetravalent actinides.

4. I have modified the standard procedure of the IAEA Clean Laboratory for the determination of U and Pu in environmental samples in order to analyze ^{238}Pu after purification on an anion exchange resin and combining alpha spectrometry with ICP-MS. The amount of ^{238}Pu is calculated from the ^{238}Pu / ^{239,240}Pu ratio – determined by alpha spectrometry – in the view of the amount of ^{239}Pu and ^{240}Pu – determined by ICP-MS. The results demonstrated that 10 fg of ^{238}Pu can be determined within 6% of total uncertainty. The ^{238}Pu determination can enhance the reliability of the final conclusions of the analysis of the safeguards inspection samples. The method has got application in the practice of the IAEA Clean Laboratory.

5. I have developed a complex method for the determination of the U isotopic composition of single particles originating from safeguards swipe samples. The method consists of several, individual procedures for (1) particle removal from swipe samples by vacuum impactor technique, (2) the identification of particles containing alpha emitting material using solid state nuclear track detectors, (3) the localization and relocalization of identified particles based on basis transformation, (4) the micromanipulation of particles and (5) the analysis of single particles (>10 μm) by LA-ICP-MS. The procedures can be combined ad-libitum. The method was used for the examination of particles originating from confiscated nuclear fuel pellets.

7. Publications related to the Ph.D. dissertation

Refereed Journal Publications

1. Mácsik, Z., Groska, J., Vajda, N., Vogt, S., Kis-Benedek, G., Kim, C.S., Maddison, A., Donohue D. (2012) *Improved radioanalytical method for the simultaneous determination of Th, U, Np, Pu and Am(Cm) on a single TRU column by alpha spectrometry and ICP-MS.* **Radiochimica Acta**, Accepted for publication

2. Mácsik, Z., Shinonaga, T. (2010) *Accuracy and precision of ^{238}Pu determination at fg level by alpha spectrometry using ^{239}Pu and ^{240}Pu amount analyzed by inductively coupled plasma mass spectrometry*. **Applied Radiation and Isotopes**, 68 2147-2152

3. Vajda, N., Törvényi, A., Kis-Benedek, G., Kim, C.K., Bene, B., Mácsik, Zs. (2009) *Rapid method for the determination of actinides in soil and sediment samples by alpha spectrometry*. **Radiochimica Acta**, 97 395-401

4. Mácsik Zs., Vajda N., Bene B., Varga Zs. (2009) *Radioanalitikai módszer fejlesztése dörzsmintákban található aktinidák elemzésére*. **Sugárvédelem on-line folyóirat**, II. évf. 1. szám 14-18

Conference papers

5. Mácsik Z., Széles É., Stefánka Zs., Vajda N. *Method development for analysis of single particles for safeguards purposes* – conference paper and presentation; **33rd ESARDA Annual Meeting – Symposium on safeguards and nuclear material management**, 16-20 May 2011, Budapest, Hungary

6. Mácsik, Z., Vajda, N., Széles, É., Katona, R. *Method development for analysis of single hot particles in Safeguards swipe samples* – conference paper and poster; **Symposium on International Safeguards: Preparing for Future Verification Challenges**, 1-5 November 2010, Vienna, Austria

7. Mácsik Zs., Vajda N., Széles É., Katona R. *Módszerfejlesztés nukleáris biztosítéki célú dörzsmintákban található egyedi forró részecskék analízisére* – conference paper and presentation; **Őszi Radiokémiai Napok 2010**, Hevesy prize special award, 20-22 October 2010, Keszthely, Hungary

8. Vajda, N., Molnár, Zs., Mácsik, Z., Széles, É., Hargittai, P., Tóth Pintér Csordás, A., Pintér, T. *Corrosion particles in the primary coolant of VVER-440 reactors* – conference paper and presentation; **Nuclear Plant Chemistry Conference,** 3-7 October 2010, Quebec City, Canada

9. Mácsik, Zs., Shinonaga, T. *Környezeti minták Pu tartalmának nagy pontosságú meghatározása biztosítéki ellenőrzések céljából* – conference paper and presentation; **Őszi Radiokémiai Napok 2009**, Hevesy prize 2nd place, 14-16 October 2009, Pécs, Hungary

10. Mácsik Zs., Vajda N., Bene B., Varga Zs. *Radioanalitikai és mikroanalitikai módszerek fejlesztése dörzsmintákban található aktinidák elemzésére* – conference paper and presentation; **Őszi Radiokémiai Napok 2008**, 28-30 October 2008, Hajdúszoboszló, Hungary

11. Mácsik, Z., Vajda, N., Bene, B., Varga, Zs. *Development of Radioanalytical and Microanalytical Procedures for the Determination of Actinides in Environmental Samples* – conference paper and presentation; **International Youth Nuclear Congress 2008** (IYNC 2008), ENEN prize, 20-26 September 2008, Interlaken, Switzerland

Conference and seminar presentations and posters

12. Mácsik Zs., Vajda N., Groska J., Széles É. *Th, U, Np, Pu és Am egymás melletti elválasztása egyetlen extrakciós kromatográfiás oszlopon* – presentation; **Őszi Radiokémiai Napok 2011**, 26-28 October 2011, Sopron, Hungary

13. Mácsik Z., Széles É., Stefánka Z., Vajda N. *Localization and analysis of single uranium particles by LA-ICP-SFMS* – poster; **European Winter Conference on Plasma Spectrochemistry**, 30 January - 4 February 2011, Zaragoza, Spain

14. Mácsik Zs., Széles É. *Módszer fejlesztése forró részecskék azonosítására és lokalizálására biztosítéki részecske-analízis céljára* – presentation; **XXXV. Sugárvédelmi Továbbképző Tanfolyam**, 27-29 April 2010, Hajdúszoboszló, Hungary

15. Mácsik, Z. *IAEA Fellowship at the Clean Laboratory, SAL - 10/11/08–08/05/09* – presentation; **Seminar in the Safeguards Analytical Laboratories (SAL), International Atomic Energy Agency (IAEA)**, 15 May 2009, Seibersdorf, Austria

16. Mácsik, Z. *Experiences on environmental sampling and analysis for safeguards purposes in Hungary* – presentation; **International Training Course on Implementation of State Systems of Accounting for and Control of Nuclear Material**, 23 June - 4 July 2008, Moscow, Rusia

17. Vajda, N., Törvényi, A., Kis-Benedek, G., Kim, C.K., Mácsik, Z., Bene, B. *Method development for the simultaneous determination of actinides using mass spectrometric and LSC techniques* – presentation; **LSC 2008 – Advances in Liquid Scintillation Spectrometry**, 25-30 May 2008, Davos, Switzerland

18. Mácsik Zs., Bene B., Vajda N.: *Környezeti minták elemzése biztosítéki (safeguards) célból* – presentation; **XXXIII. Sugárvédelmi Továbbképző Tanfolyam**, 6-8 May 2008, Hajdúszoboszló, Hungary

19. Mácsik, Z., Vajda, N., Surányi, G.: *Method development for the determination of actinides and studies on actinide speciation in coolant* – poster; **ACTINET Plenary Meeting**, 18-20 March 2008, Avignon, France

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